

✓STUDIES IN REACTION KINETICS IN PRESENCE OF MICELLE-FORMING SURFACTANTS

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in Partial Fulfilment of the Requirements
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by
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to the
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STATEMENT

I hereby declare that the work presented in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor Sarvagya S. Katiyar.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.



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PREFACE

Recently, there has been a growing interest in the studies of chemical reactions in presence of micelle-forming surfactants because of possible potential application of these studies in understanding certain biological processes, analytical determinations, stabilization of medicines in aqueous medium, organic synthesis, and in stabilization of products of certain photoredo reactions used as possible means of solar energy conversion and storage. Numerous and diverse reactions viz., hydrolysis, thio-lysis, nucleophilic substitutions and several other types of reactions have been studied in presence of micelle-forming surfactants. Mathematical formulations for the analysis and interpretation of data have also been proposed, which have limitations of their own.

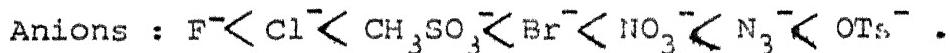
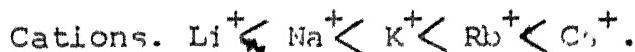
These studies were started with the aim of understanding the micellar effects in general and the micellar effects on the reactions of carbonium ions, generated from triphenylmethane dyes with nucleophile hydroxide ion, in particular. Accordingly, this thesis deals with the (a) Formulation of reaction kinetics in presence of micelle-forming surfactants; (b) Experimental studies on the reactions of triphenyl methyl carbonium ions with hydroxide ions in presence of micelle forming surfactants and (c) Analysis of our data and the data available in the literature for the effects of counterions on the micelle catalysed/inhibited reactions, using our model. To a good extent, the present work

has contributed towards the understanding the reaction kinetics in presence of micelle forming surfactants. It has been pointed out that for the reaction rates to be influenced in presence of micelle-forming surfactants one or more reactants must possess hydrophobicity and the possession of hydrophobicity, in principle, should alter the micellar properties of the surfactants.

Model schemes, based upon the participation of substrate, detergent, additive and/or reactant species in the formation of catalytic aggregates, have been presented and the method for analysis of micellar data for chemical reactions have been developed. The experimental studies in the reactions of setoglaucine (SG^+), brilliant green (BG^+) and malachite green (MG^+) carbonium ions with hydroxyl ion in presence of cationic micelle-forming surfactant cetyltrimethylammonium bromide (CTAB) and anionic micelle-forming surfactant sodium dodecyl sulphate (SDS). viz., effects of concentrations of detergent, substrate reactant, counter ions and organic solvents in micellar environment have been reported. The thermodynamic quantities of activation for the reactions have been evaluated and compared with corresponding values in aqueous media. Micellar effects in presence of SDS have been assigned to stabilization of ground state with respect to transition state and the nonapproachability of hydroxyl ion to the carbonium ions, in the reaction systems. In presence of CTAB the ground state of the reactions gets destabilized with respect to the transition state and the approach of the hydroxyl ions to carbonium ions in the catalytic aggregates is facilitated resulting

in the observed catalysis. The effect of inert counter ions on a reaction is explainable in terms of the replacement of reactant ions by them from the vicinity of catalytic micelles and the alteration in thermodynamic parameters of the reaction. A generalized background for the understanding of the effect of organic solvents on micellar catalysis in view of current theories of the effect of solvents on chemical reactivities has been highlighted.

The analysis of the data has been extended for the effects of counterions on micellar catalysis available in the literature. It has been concluded that the effect of addition of counterions in the reaction system does not always result in the replacement of the substrate from the catalytic aggregates. The alteration in the reactant concentration in the vicinity of aggregates does play a significant role for the observed effects. The values of exchange factor as postulated in the thesis could be taken as a measure of the effectiveness of counter ions in altering overall micellar influence. This is in the order:



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I.1 IMPORTANCE OF STUDY

Surfactants, surface active agents or detergents continue to be utilized increasingly in various fields such as, corrosion inhibition, ore floatation, textile and paper processing, lubrication, detergency, tertiary oil recovery, polymerization reactions, phase transfer catalysis, photography and preparation of protective emulsions for the food, cosmetic and pharmaceutical products.¹⁻¹⁵ The information concerning the classification, methods of preparation, analysis and purification and sources of procurement of various surface active agents has been extracted and compiled.¹⁶

The presence of a micelle-forming amphipathic substance in most of the reaction systems result, in the perturbation of thermodynamic parameters of the reaction and the concentrations of reactants get reorganised at the reaction sites with the result that catalysis or inhibition is exhibited. Recently, there has been a growing interest in the studies of chemical reactions in presence of micelle-forming surfactants because of possible potential application of these studies in understanding certain biological processes, analytical determinations, organic synthesis and in stabilization of products of certain photoredox reactions which are viewed as possible means of solar energy conversion and storage. Numerous and diverse reactions viz., hydrolyses, thio-lyses, aminolyses, nucleophilic substitution and several other types of reactions have been studied in presence of micelle-forming surfactants. Mathematical formulations for the analysis and

interpretation of kinetic data concerning micellar influence on chemical reactions are in the process of development. The extensive literature generated, as a result of worldwide interest has been the subject of several comprehensive reviews.^{1,3,16-25}

A great many biological processes occur in or involve amphiphatic environment. These include enzyme - catalysed reactions, assembly of multienzyme complexes, facilitated transport of ions and molecules, cellular adhesion and recognition, generation and conduction of nervous impulses, and sensory reception and transduction etc. Understanding of these phenomena at molecular level is of great general importance for several reasons. The belief that this understanding could be facilitated, at least in part, by the knowledge of micellar influence on chemical reactions is now gaining ground. The resemblance between enzyme- and (pre)micelle affected reactions has been contemplated on the basis of the observations of saturation kinetics, substrate specificity (in some cases), lack of homogeneity in submicroscopic surface of (pre)micelles as well as that of enzyme, and the fact that both (pre)micelles and enzyme bind the substrate in a noncovalent manner prior to catalytic step.¹⁶⁻³¹ Recently, Nagyváry and Fendler³²⁻³⁶ have attempted to explain prebiotic chemical evolution by proposing that surfactant aggregates or micelles at the primitive ocean surface could have provided appropriate compartments for the selective uptake of amino acids and might have as well catalysed the formation of polypeptide and polynucleotides. It may be pointed out that micelles, just like most prebiotic

models, have shortcomings.³⁶⁻⁴¹

Though, an increasing number of reports are being published in the studies concerning the effect of micellar environment on kinetics of chemical reactions, only a few of these are concerned with the application of micellar effects in the area of analytical chemistry. Spurlin and Linze^{42,43} have reported that the sensitivity, accuracy, reproducibility and the efficiency of quantitative determination of cyanide ion could be enhanced by spectrophotometric method using 5,5'-dithiobis(2-nitrobenzoic acid), commonly referred to as Ellman's compound, and by photofluorometric method using potassium salt of 1,4-naphthoquinone-2-sulfonic acid as reagents in the micellar environment of cetyltrimethylammonium bromide. Vokhande and Munshi^{44,45} have reported the micro-determination of certain lanthanides and actinides using triphenylmethane dyes as reagents in presence of micelle-forming surfactants.

The utilization of surfactants as reaction media affects rates, products and in some cases stereochimistry of the reactions.¹⁶⁻²⁵ Mechanistic work on micellar effects is typically done using reactant concentrations much below than those required for normal preparative work. However, surfactants are used in emulsion polymerization, where the micelles control chain initiation and growth, and in some organic reactions.^{6,49} Micellar solutions in some cases have proved superior to organic solvents as reaction media to obtain better yields.⁵⁰⁻⁵² For example photochemical crossed-cycloaddition reaction of acenaphthylene with

acrylonitrile in micellar environment was more effective than in benzene to give better yield of the addition product, especially by adding 1,3,5-heptatriene as quencher. Reger and Marib⁵⁷ have studied the effect of micelles on the $K_3[Co(CN)_6]^{4-}$ catalysed hydrogenation of 2-methylbutadiene, 2,3-dimethylbutadiene and trans-1,3-pentadiene to improve the yield of the products. The finding of Shinkai *et al.*^{53,58} that nonenzymatic oxidation of nitroalkane carbanions by isoalloxazines, flavin analogues, is remarkably facilitated in presence of cationic micelle-forming surfactants, may be applied to oxidation of other carbanions, leading to new synthetic procedures.

Photoredox reactions in which an electron is transferred from a low energy donor to a high energy acceptor, using visible light are currently receiving wide attention as possible means of solar energy conversion and storage and also as simple models to simulate photosynthetic electron transport.^{16,58,59} In the photoredox reaction:



a large fraction of incident light energy may be initially converted into chemical energy. The practical application of such a system is hampered by the fact that the thermodynamically favourable back reaction of redox products occurs rapidly in homogeneous solvents. Therefore, the chemical potential available in the radical ion pair $A^-...D^+$ is degraded thermally. A promising approach

to overcome this problem is to employ charged surfactant aggregates such as micelles or vesicles in aqueous solution as a reaction media.⁶⁰⁻⁷⁵ A microheterogeneous system, such as micelles, containing a strongly absorbing photo-catalyst, offers several advantages over homogeneous solvent systems. Firstly, most of the water insoluble sensitizers can be used. It is possible to use high concentrations of the sensitizer without appreciable loss in the overall efficiency by keeping the solute to micelle ratio fairly low. Secondly, the low ionization threshold in micelles enables usage of visible light. In the third place, the rate of geminate ion-recombination can be kept low in micelles. Studies of electron transfer reactions in micelles using triplet excited states of molecules as donors or acceptors and also those involving hydrated electrons and solutes indicate that with proper choice of conditions, the undesirable back reactions could be reduced to some extent. Chemists, especially kineticists are probably fascinated when catalysis in reaction rate is observed but the ability of micelles to inhibit reactions is of great practical importance in stabilizing aqueous solutions of labile solutes for extended storage.

I.2 CHEMICAL REACTIONS STUDIED I. MICELLAR ENVIRONMENT IN AQUEOUS MEDIA

The kinetic studies of chemical reactions in micellar environment have followed two main streams viz., (i) the effect of substrate micellization and (ii) the effect of micelle-forming surfactants on the reaction rates.

It was found that reaction rates sometimes change very sharply when hydrophobic groups cause a substrate to micellize. For example, acid hydrolysis of monoalkyl sulfates is independent of an increase in length of *n*-alkyl group up to *n*-pentyl, but longer alkyl groups cause the substrate to micellize and there is, then, a sharp increase in reaction rate. The rate enhancement is readily understandable in terms of the increased concentration of ionic reactant in the Stern layer of the substrate micelle.⁷⁶⁻⁸⁴ There are several systems in which substrate micellization controls the stereochemical course of reactions.⁸⁵⁻⁸⁶ The nitrous acid deamination of chiral primary amines generally involves extensive racemization with partial inversion of the product alcohol. However, if the alkyl group of the amine is sufficiently hydrophobic, for the substrate to micellize, the product has a partially retained configuration, because the micellization causes the intermediate carbocation or ion pair, to suffer predominantly front side attack by water molecules of the solvent. The stereochemical course of reaction is also very sensitive to added salts,^{86,87} where anions cluster around the micellized alkyl ammonium ion and thereby affect the attack of water.

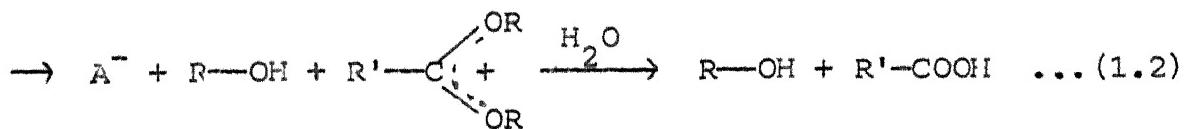
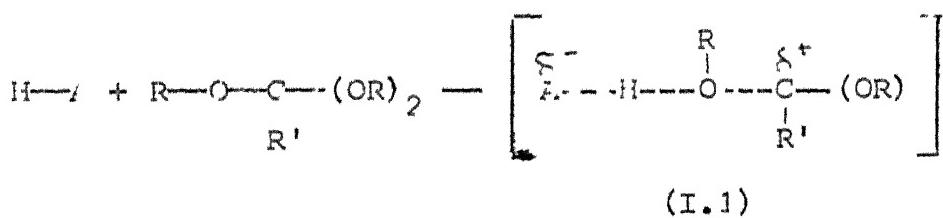
Earlier studies of chemical micellar effects were done on acid-base equilibria. The protonation of an indicator base was affected by micelle-forming surfactants, and these observations led to the formation of a sign rule which explained the effects in terms of the electrostatic interactions between ionic micelles

and the ionic species in the acid-base equilibria. This simple electrostatic theory has since been applied to reaction rates and equilibria and considerable efforts have been devoted to explore its limitations. This led to the discovery of the significance of hydrophobic interactions in micellar effects. 16-25, 87-88

I.2.1 Micellar Effects of Hydrolyses, Solvolyses and Aminolyses

Acid catalysed hydrolyses of orthoesters and acetal, pH dependent, general and specific acid catalysed and general and specific base catalysed hydrolyses and solvolyses reactions of cyclic esters, sulfates, phosphates, chlorides, Schiff's bases and certain other substrates have been studied extensively in presence of micelle-forming surfactants.

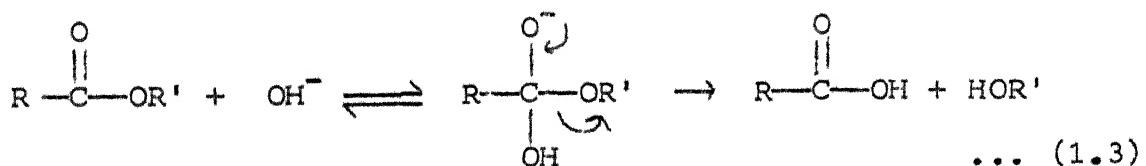
The mechanisms of ortho-esters hydrolyses have been summarized and discussed by several authors. 27, 89-92 The general acid catalysed hydrolysis of orthoesters involves proton transfer from the acid to an ester oxygen atom followed by the rate determining cleavage of carbon-oxygen bond resulting in the formation of an alkoxy carbonium ion intermediate which rapidly decomposes to products.



The most probable mechanism of rate determining step involves a

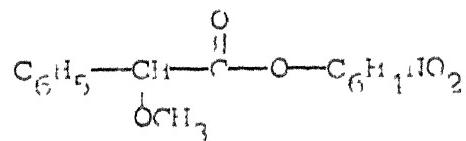
transition state such as (I.1) in which proton transfer either proceeds or is concerted with cov lert bond breaking. The effect of a number of cationic, anionic and nonionic micelle-forming surfactants on the acid hydrolyses of various orthoesters has been investigated.⁹³⁻¹⁰¹ These studies show that th. micellar catalysis exhibits a considerable substrate specificity e.g., the rate of hydrolyses of methyl orthobenzoate and substituted methyl orthobenzoates are accelerated by maximum rate factors ranging from 80 to 115 whereas the corresponding values for ethyl orthopropanoate and ethyl orthopentanoate are 2.3 and 4.6 respectively, which are relatively very small and the hydrolysis of ethyl orthoformate is not catalysed by sodium dodecyl sulfate. The structure and the charge type of the surfactant also influences the extent of overall micellar catalysis. Studies of Dunlop and Cordes⁹⁶ show that catalysis of these reactions in micellar environment is enthalpy controlled. The studies concerning the effect of substituent group in the substrate have also been reported.

A number of texts and reviews deal with the specific mechanisms involved in pH dependent carboxylic ester hydrolyses and solvolyses.¹⁰²⁻¹⁰⁶ Base catalysed hydrolysis of carboxylic esters proceeds by bimolecular attack of hydroxide ion on the carbinol group forming a tetrahedral intermediate following by elimination with acyl oxygen fission:

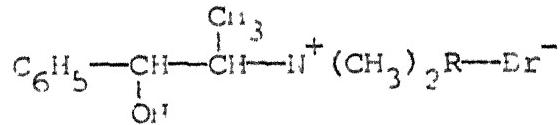


The effect of micellar environment on rate and the activation parameters of the reaction of a number of carboxylic esters hydrolysis has been scrutinized. The influence of increasing substrate hydrophobicity, surfactant chain length and the effect of chemically inert counter ions on the micellar catalysis has also been studied.^{103,119}

Stereospecificity in micellar catalysis has been examined on the hydrolysis of optically active and racemic mandelic acid esters (I.2) in presence of optically active surfactants¹¹⁰ (I.3).



(I.2)



(I.3)

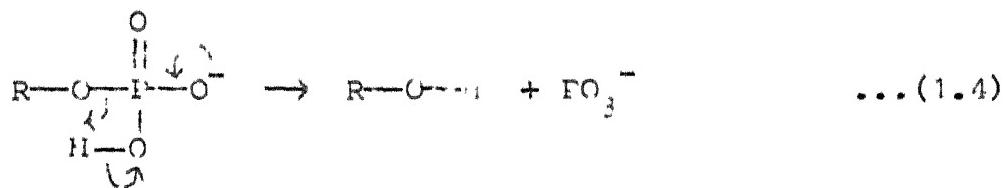
For (I.3a), R = CH₃(CH₂)₉

and For (I.3b), R = CH₃(CH₂)₁₁.

The order of catalytic efficiency of D(-) surfactant (I.3a) for the hydrolysis of (I.2) was D(-) > L(+) > DL. These results were rationalized by assuming that more molecules of (I.2) than one are solubilized by micelle and that two enantiomers perturb the micelle in different fashion.¹²⁰ It is expected that investigations of the properties of optically active micelle forming surfactants would prompt additional searches into stereospecific

micellar catalysis.^{121,122}

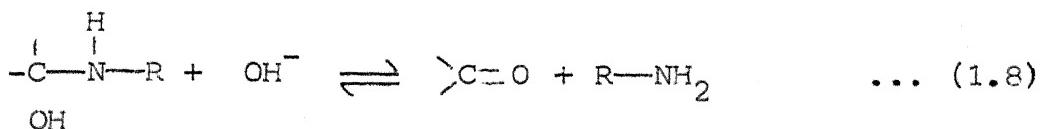
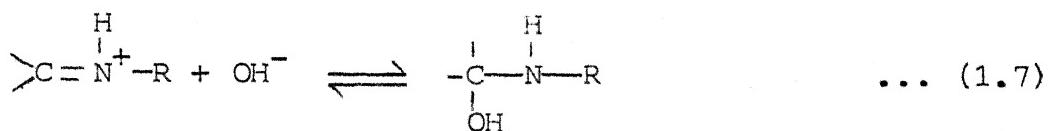
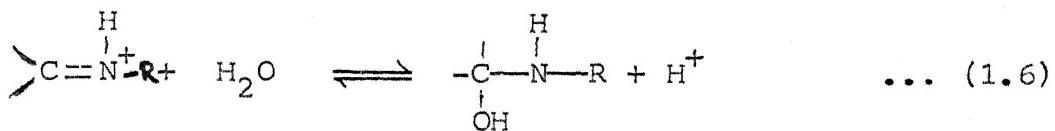
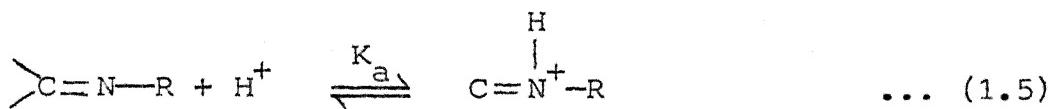
In recent years considerable interest has been stimulated in mechanisms of hydrolysis of sulfate and phosphate esters primarily as a consequence of their importance in biochemical systems. Since sulfuric and phosphoric acids are di- and tribasic, successive substitution of acidic hydrogen atoms by alkyl or aryl groups can result in the formation of mono-, di-, or triesters. The incompletely substituted sulfuric and phosphoric acid esters can exist in various extents of protonation depending upon the pH of the solution and thus several probable mechanisms have been postulated for each type of ester depending upon the substituents and the acidity of the medium.^{26,27,106,123} The effects of various parameters viz., concentrations of surfactant, substrate, counter ions, temperature and pH have been studied by a number of workers on these reactions.¹²⁴⁻¹³⁹ Cordes²⁵ has argued that micellar catalysis of phosphate ester hydrolysis is derived from medium effects as opposed to entropic ones. Phosphate ester monoanions hydrolyse via unimolecular elimination of a metaphosphate ion:



Although phosphate monoanions are readily incorporated into micellar phase of cationic surfactants, this does not result in an appreciable alteration in hydrolysis rate.¹²³ The ~~del~~ phosphate ester dianions in which the leaving group contains strong electron attracting groups also hydrolyse via unimolecular elimination of

metaphosphate. In this case, however, cationic micelle-forming surfactants are good catalysts for hydrolysis.^{123,132} For example, the rate of hydrolysis of 2,5-dinitrophenylphosphoric dianion is approximately 25 times more rapid in presence of an optimal concentration of hexadecyltrimethylammonium bromide than in water. The loss of the metaphosphate anion from a phosphate ester dianion involves a dispersal of two negative charges. Consequently, one may argue that the catalytic driving force involves destabilization of the substrate relative to the transition state by the relatively nonpolar micellar environment. This conclusion is consistent with the fact that the rate of hydrolysis of phosphate ester dianions is significantly increased with a decrease in solvent polarity in the absence of micelle-forming surfactants. The basic hydrolysis of phosphonates is analogous to that of a phosphate triester.¹⁴⁰

The interest in the mechanisms of Schiff base hydrolysis emanates largely from the fact that the formation and decomposition of Schiff base linkages play an important role in a variety of enzymatic reactions e.g., carbonyl transfers involving pyridoxal phosphate, aldol condensations, β -decarboxylations and transaminations. The mechanisms of formation and hydrolysis of biologically important Schiff bases and imine intermediates have been discussed by Bruice and Benkovic²⁶ and by Jencks.²⁷ The mechanisms for the hydrolysis of m- and p-substituted benzylidene, 1,1-dimethylethylamines in the entire pH range have been discussed¹⁴⁰ in terms of Equations (1.5) to (1.8):



Micellar effects on hydrolysis reaction of Schiff bases in presence of ionic as well as nonionic micelle-forming surfactants have been investigated and the results were qualitatively interpreted on the basis of the distribution of reagents and the perturbation of thermodynamic parameters of the reaction.^{93, 142-144}

The reaction of several amines with 2,4-dinitrophenylsulfate in presence of cetyltrimethylammonium bromide, sodium dodecyl sulfate, Igepal and other micelle-forming surfactants is also reported.¹³⁰

I.2.2 Micellar Effects on Aliphatic and Aromatic Nucleophilic Substitution

Nucleophilic substitution reactions have been extensively investigated and mechanisms have been discussed in several books.^{106, 145} The rate determining step of substitution reactions at aliphatic carbon atoms can be either unimolecular or bimolecular. Nucleophilic aromatic substitution on the other hand, most frequently

involve the formation of an intermediate or its decomposition can be rate determining. Both aliphatic and aromatic substitution often involve the formation or the destruction of charged species, and the changes in the magnitude and the distribution of the charges between the initial state and the transition state have been correlated with medium effects. Consequently, the numerous charge changes, theoretically possible for nucleophilic substitution could serve as fertile ground for studying the effects of micelle-forming surfactants on the rate of these reactions.

A large number of nucleophilic substitution reactions have been studied in micellar environment and from the available data it appears that micellar effects are observed when one of the reactants is charged.^{110,146,164} However, it is conceivable that micellar effects on nucleophilic reactions between neutral organic molecules can be found for reactions in which the distribution of reactants between the micellar and bulk phases and the reactivities therein differs considerably.

Micellar effects on the reaction of carbocations with nucleophiles have also been investigated and the data have been interpreted in terms of the disposition of the reagents at the reaction sites and the modification in the activation parameters of the reactions.¹⁶⁵⁻¹⁶⁷ In one of the earliest studies Duynstee and Grunwald¹⁶⁸ found that rate and equilibrium constants for the addition of hydroxyl ion to stable triphenylmethyl-carbonium ions, such as crystal violet, are subject to alteration by micelle-forming surfactants. The conclusions have been confirmed and

amplified further in several subsequent investigations by Albrizzio et al.¹⁶⁹ Bunton et al.,¹⁷⁰ and by Patel and Katiyar.^{171,172}

I.2.3 Micellar Effects on Other Chemical Reactions

Micellar effects on several other reactions viz. Cannizaro reaction,¹⁷³ base-catalysed hydrolysis of α,β -unsaturated ketones,¹⁷⁴ synthesis and hydrolysis of benzylidene aniline,^{174,175} acid catalysed iodination of acetone,¹⁷⁶ base catalysed H-D exchange reactions of alkyl dimethyl sulfonium halides,^{177,178} hydrolysis of 2-t-butyl-3-phenyloxazirane and N-t-butylbenzaldoxime,¹⁷⁹ decarboxylation of substituted carboxylate ions¹⁸⁰⁻¹⁸² racemization of biphenyl,¹⁷⁵ nitrous acid deamination,¹⁸⁴⁻¹⁹⁶ electrophilic coupling reactions,¹⁵⁷ thiol-thiamine disulfide exchange reaction,¹⁸⁷ reaction of hydroxyl ion with tetranitromethane,¹⁸⁸⁻¹⁹¹ cupric ion incorporation into porphyrin esters,¹⁸⁴ ¹⁹²⁻¹⁹⁴ hemin equilibria,¹⁹⁷⁻¹⁹⁸ conversion of ammonium cyanate to urea,¹⁹⁵ mercury(II) induced aquation¹⁹⁶ of $\text{Co}(\text{NH}_3)_5\text{Cl}^{+2}$, radical and excited state reactions,¹⁹⁹ Hoffmann elimination reaction¹⁹⁹ etc. have also been studied.

I.3 MATHEMATICAL FORMULATIONS FOR QUANTITATIVE ANALYSIS AND INTERPRETATION OF KINETIC DATA

In the earlier phase of studies the investigators devoted their efforts to the accumulation of kinetic data for numerous chemical reactions in presence of micelle-forming surfactants.¹⁶⁻²⁵ However, it has been tempting to provide an explicit quantitative explanation to account for the principle features of micelle effected reactions.

Heitmann²⁰⁰ on the basis of empirical calculations of concentration effects on the reaction rate in presence of micelle-forming surfactants was able to predict qualitatively, that (i) the presence of micelle-forming surfactant causes an increase in the reaction rate if the reactants are enriched in one phase, namely micellar or the bulk phase. In the latter case the effect is expected to be small. (ii) If one reactant is enriched in one phase and the concentration of other reactant in this phase is lower than its average value in two phases, the reaction is retarded in presence of micelle-forming surfactants. (iii) If the concentration of one reactant differs in two phases while of other reactant are equal over the whole system, then no alteration in the reaction rate would be observed upon the introduction of micelle-forming surfactants in the reaction system.

These calculations were further extended and elaborated by Berezin et al.^{154,175} to compare the effectiveness of micellar catalysis in first, second and third order reactions. The salient features of these calculations for micellar effects were that: (1) a rigid structure was considered for micelles, (2) the modification in concentrations of the reactants as a result of the presence of micelles in the reaction system was taken into account, (3) the effect of micelles on reaction rate due to perturbation of activation parameters of the reactions was argued to be superfluous, (4) the effects of additives i.e., counter ions etc. could not be treated on the basis of these calculations.

Employing certain simplifying assumptions Menger and portnoy⁷⁸ were able to explain, semiquantitatively, the sigmoidal increase in the rate constant with increasing surfactant concentration. Such behaviour is seen for unimolecular and for a few pseudo first reactions in presence of micelle-forming surfactants. On the other hand, the reactions which are second order or higher order, usually exhibit optimal rate at some surfactant concentration above which rate decreases with increasing surfactant concentration. Bunton et al.¹²³ have extended this model to explain the effects of inhibitors which had found only limited applicability. Another model assuming rigid structure of micelle and the distribution of reactants in two phases was put forward by Srirahama.²⁰¹ This model could not be applied to explain the relative differences in various counter ions in altering the over all efficiency of micellar effects on chemical reactions. Funasaki^{202,203} has treated micellar effects by determining the reactant concentration in the stern layer of micelles on the basis of equilibrium constant of certain dyes in presence of micelle-forming surfactants. Romsted²⁰⁴ has attempted to explain the rate vs surfactant concentration profile by assuming exchange between reactive and nonreactive counter ions at micellar surface and the constancy of the degree of counter ion dissociation of the micelles.

The constancy of degree of ionization has recently been suspected.²⁰⁵ Further, it is authors view that the degree of counter ion dissociation of catalytic aggregates in presence of

different electrolytes might be different, and this difference in charge neutralization of the catalytic aggregates by counter ions might play a significant role in determining the overall efficiency of micellar catalysis in presence of different counter ions. It is important to mention here that all the models described earlier assume that the alterations in the aggregational properties of the surfactant and consequently the micellar properties are insignificant. However, the phenomena viz., micellization of hydrophobic substrates by themselves,^{76-84,167} comicellization of organic substances¹⁷ with surfactants e.g., tosylate ion,²⁰⁶ interactions of oppositely charged dyes with surfactants²⁰⁶ and the observation of catalysis well below critical micelle concentrations^{16,171,172} clearly establish that the perturbation caused by the substrates in altering micellar properties of the detergent in presence of various species viz., reactant, electrolytes/buffers and the solvents, are definitely important. These findings suggest that hydrophobic substrate might comicellize with the surfactant molecules to produce catalytically functional aggregates. The participation of counter ions, reactant and other additives in the formation of such aggregates might also be important.

Available data on reaction kinetics in presence of micelle-forming surfactants show that for the reaction rate to be affected in the micellar environment one of the qualifying criteria is that one or more reactant must possess hydrophobicity and the fulfilment of such criterion should result in the alteration in

the micellar properties of the detergent. Piszkiewicz has recently proposed another model in which the effect of counter ions on micellar effects has been overlooked.

I.4 OBJECTIVES OF THE PRESENT STUDY

The investigations presented in this thesis were started with the aim of understanding the micellar effects on chemical reactions in general, and micellar effects on the reaction of carbonium ions, generated from triphenylmethane dyes, with nucleophile hydroxyl ion, in particular.

The effect of micelle-forming surfactants viz., cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) on the reaction of setoglaucine (SG^+), brilliant green (BG^+) and malachite green (MG^+) carbonium ions with hydroxyl ion was investigated. The influence of various parameters viz., concentrations of detergent, reactant, substrate, organic solvents and counter ions and the effect of temperature on these reactions, to evaluate and compare activation parameters of the reactions in micellar environment to that of aqueous media, was investigated.

Model schemes²⁰⁷ have been proposed which take into account the participation of substrate, counter ions and/or reactant alongwith the detergent species in the formation of catalytic aggregates. The experimental data obtained by us and the data available in the literature have been analyzed on the basis of these schemes. These interpretations have led to the following conclusions:

(1) Substrate, counter ions and/or reactant do play a significant role in determining the nature and composition of the catalytic aggregates formed in micellar environment.

(2) The degree of ionization of catalytic micelles formed by the participation different substrates in presence of different reactant, counter ions and other species in the reaction system may not be the same.

(3) The effect of inert counter ions may be treated quantitatively in terms of the displacement of the reactive counter ions by them from the vicinity of catalytic aggregates.

(4) Reorganization of reactants as well as the alteration in activation parameters of the reaction are the factors responsible for observed micellar effects on chemical reactions. Other characteristic features of micellar effects are described, in other chapters of the thesis.

The studies concerning the effect of organic solvents on the reaction rate in micellar environment have been scanty. A generalized background for the understanding of the effect of organic solvents on the kinetics of chemical reactions in presence of micelle-forming surfactants in the light of current thinking²⁰⁸ of solvent effects on chemical reactivities i.e., selective solvation of reactants and the motion of solvent molecules along the reaction coordinates, has been presented. Various factors which possibly determine the overall effect of organic solvents on the influence of micelle-forming surfactants on the reaction of

triphenylmethyl carbonium ions with hydroxyl ion have been attempted to be distinguished.

I.5 FUTURE SCOPE OF THE PRESENT WORK

Formulation of model schemes and subsequent analysis of the micellar data for reaction kinetics of several reactions provides the average numbers of substrate, detergent and counter ions etc. which associate to form catalytically functional micelles. The actual overall picture concerning the composition of these aggregates still remains to be searched out. Recently, numerical methods for the characterization of micellar solutions based on Poission-Boltzman equations have appeared.²⁰⁹ The observed micellar properties of these aggregates could be analyzed on the basis of these methods to obtain overall charge and consequently the overall picture of micellar aggregates in presence of the concerned substrate, detergent, counter ions and/or the reactant. Model calculations proposed by Stenius et al.²¹⁰ based upon the work carried out by Ruckenstein and Nagarajan,²¹¹ Israelachvili et al.²¹² and Tenford,²¹³ following the evaluation of partition functions for various interactions in micellar environment might be applied to a comicelles of substrate and detergent which might provide an insight into the observed micellar effects on chemical reactions in terms of the microstructure of the reaction systems.

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CHAPTER II

FORMULATION OF REACTION KINETICS IN PRESENCE OF MICELLE-FORMING SURFACTANTS

II.1 ABSTRACT

The presence of micelle-forming surfactants introduces microheterogeneity in the reaction system. Consequently, the concentrations of the species, present in the reaction system, get reorganized at the reaction sites and the thermodynamic parameters of the reaction are perturbed, which is manifested in the form of observed micellar effects viz., catalysis or inhibition of chemical reactions. It is proposed that the kinetic data for micellar effects for the reaction between a hydrophobic substrate and a hydrophilic reactant could, in general, be described by either of two model schemes based upon the postulation that in the reaction system charged or neutral species viz., detergent, substrate, additive i.e., counter ion etc. and/or reactant associate to form catalytically functional micelles. The first scheme is applicable to cases where mutual competition between reactant and additive for sites in or on the catalytic micelles is absent, whereas the second scheme can be applied to reactions where reactant and additive species do compete for sites in or on the complexed aggregates. Equations dealing with the formulation of these schemes have been derived and methods for the analysis of micellar data have been developed.

II.2 INTRODUCTION

The present formulation of reaction kinetics in presence of micelle-forming surfactant is based upon the proposition that in the reaction system the detergent, substrate, additive i.e., counter ion etc. and/or the reactant species aggregate to form

catalytically functional loose complex which may be called catalytic micelle. The process of aggregation has the effect on the organization of the reacting species at the reaction sites and on the thermodynamic parameters of the reaction which are perturbed in micellar environment. Consequently, the chemical reaction is either catalysed or inhibited.^{1,2} The concentration of any of the species in complexed phase is assumed to be in dynamic equilibrium with its concentration in aqueous bulk phase. The postulation is supported by the observation of micellar catalysis well below critical micelle concentration of the surfactants by Patel and Katiyar,^{3,4} Bunton *et al.*,⁵⁻⁹ Bruice *et al.*¹⁰ Albrizzio *et al.*¹¹ and by Reeves.¹² Other observations supporting such a proposition are pointed out in Chapter I.

II.3 MODEL SCHEMES

Consider a reaction system containing charged or neutral species viz., detergent (D) hydrophobic substrate (S), hydrophilic reactant (I) and additive (A). Let the following terms represent the probable interactions:

H_{DS} : denotes hydrophobic interaction between substrate and detergent.

E_{DS} : denotes electrostatic interaction between substrate and detergent.

E_{DA} : denotes hydrophobic or electrostatic interaction between detergent and additive.

E_{DI} : denotes electrostatic interaction between detergent and reactant.

+ : represents presence of favourable interactions.

- : represents presence of unfavourable interactions.
- 0 : represents absence of any type of interactions.

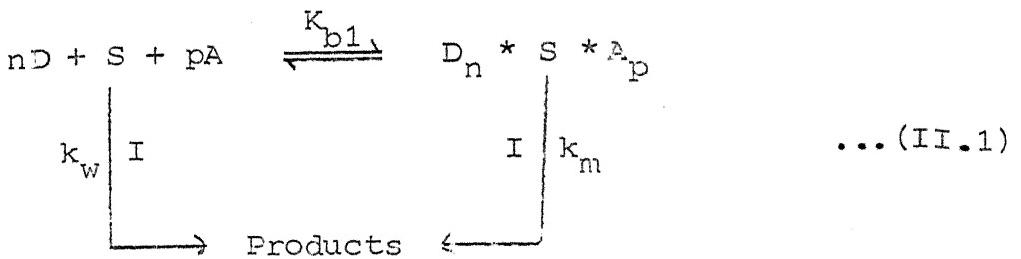
Now, assuming the interactions H_{DS} and EH_{DA} to be favourable, and examining the nature and weightage of other interactions, Table II.1 may be constructed to reflect the nature of the aggregates present in the reaction system.

The aggregates corresponding to Sl.No. 2, 4 and 6 in Table II.1 may not be of any consequence to micellar catalysis where substrate does not appear in the complex. This is exemplified¹⁴ by the effect of the detergent sodium dodecyl sulfate on the acid hydrolysis of methyl ortho-benzoate and methyl ortho-formate. The former reaction is catalysed by the presence of SDS in the reaction system whereas the latter reaction is unaffected under identical reaction conditions. The absence of micellar effects has been assigned to the inability of methyl ortho-formate to get incorporated into the complexed micellar phase due to lack of hydrophobicity in this molecule. The micellar data may, therefore be explained by assuming the formation of either of the two types of aggregates, one containing detergent, substrate and additive and other involving the participation of detergent, substrate, additive as well as reactant species in its formation.

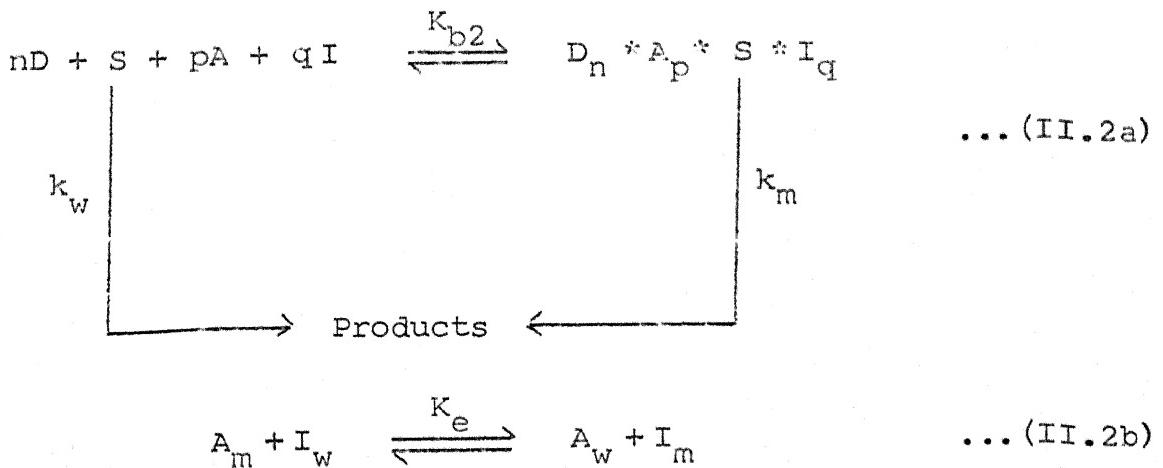
Following two schemes may be proposed for the analysis and interpretation of kinetic data in presence of micelle forming surfactants:

Table III.1. The probable nature of catalytic aggregates present in a reaction system containing a hydrophobic substrate, a hydrophilic reactant and an additive, i.e., counter ion.

Sl. No.	H _{DS}	E _{DS}	H _{DS} vs E _{DS}	E _{DI}	E _{DA}	Possible species present in the aggregates formed
1.	+	-	H _{DS} > E _{DS}	-	+	D, S, A
2.	+	-	H _{DS} < E _{DS}	-	+	D, A
3.	+	-	H _{DS} > E _{DS}	+	+	D, A, S, I
4.	+	-	H _{DS} < E _{DS}	+	+	D, A, I
5.	+	-	H _{DS} > E _{DS}	0	+	D, S, A
6.	+	-	H _{DS} < E _{DS}	0	+	D, A
7.	+	+	H _{DS} ≈ E _{DS}	-	+	D, S, A
8.	+	+	H _{DS} < E _{DS}	+	+	D, S, A, I
9.	+	+	H _{DS} > E _{DS}	0	+	D, S, A
10.	+	0		-	+	D, S, A
11.	+	0		+	+	D, S, A, I
12.	+	0		0	+	D, S, A

Scheme II.1

Scheme II.1 is applicable to cases where additive does not compete with the reactant for site in or on the catalytic micelles.

Scheme II.2

Scheme II.2 could be applied for the analysis of micellar data for the kinetics of reactions where additive does compete for the sites in or the catalytically functional micellar aggregates. In this process of competition the reactant concentration in the vicinity of catalytic micelles decreases continuously with the increasing additive concentration and vice-versa. The concentration of additive and reactant in two phases is assumed to be related through the process of exchange. The value of pseudo

first order rate constant in complexed phase will thus be dependent upon the concentrations of reactant as well as that of additive in the reaction system.

In these schemes k_w and k_m are pseudo first order rate constants for the reaction of free and complexed substrate respectively. K_{b1} and K_{b2} are equilibrium binding constants for Scheme II.1 and Scheme II.2 respectively. K_e is the exchange constant governing the competition between additive and the reactant for sites in or on catalytic micelles. In the actual reaction system multiple, sequential, equilibrium steps are involved in which detergent, substrate, additive and/or reactant aggregate to form catalytic micelles. They are presented here as a single association step for the sake of mathematical convenience.

II.3 DERIVATION OF EQUATIONS

It is apparent that the presence of micelle-forming surfactant has the effect of introducing microheterogeneity in the reaction system. Consequently, various species present in the solution get distributed into free and complexed fractions. The observed reaction rate in such a microheterogeneous system may be given by the sum of rates in aqueous bulk phase and complexed phase. Thus,

$$\text{Observed reaction rate} = \text{reaction rate in aq. bulk phase} + \text{Reaction rate in complexed phase} \quad \dots (2.1)$$

$$k_\psi (C_S) = k_w (C_S)_w + k_m (C_S)_m \quad \dots (2.2)$$

where k_{ψ} is observed pseudo first order rate constant, C_S is substrate concentration and the subscripts t, m and w refer to total, complexed and free species respectively. Absence of subscripts, later, corresponds to species remaining uncomplexed.

It is assumed that there is continuous exchange of species in free and complexed phase and thus in the steady state, catalytic micelles and other species in reaction system remain in dynamic equilibrium with one another. The values of equilibrium constants, K_{b1} or K_{b2} are governed by intrinsic nature of the species present in the reaction system. If these loose complexed aggregates are assumed to be distributed throughout the volume of the reaction system, then one may write,

$$k_{\psi} = F_w k_w + F_m k_m \quad \dots (2.3)$$

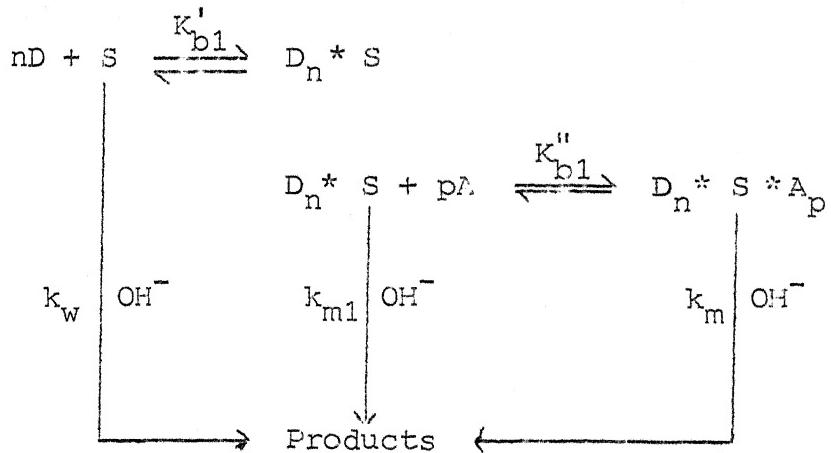
where F_w and F_m represent unbound and complexed fractions of the substrate.

III.3.1 Scheme III.1

The overall binding constant K_{b1} for the reaction Scheme III.1, by the application of law of mass action may be written as follows:

$$K_{b1} = \frac{(C_{agg2})}{(C_D)^n (C_S)^m (C_A)^p} \quad \dots (2.4)$$

The Scheme III.1 may be supposed to involve following two steps:



In the first step the detergent and the substrate associate to form $D_n^* S$ which interacts with the counter ions present in the reaction system to form the aggregates of the type $D_n^* S * A_p$. k_{m1} and k_m represent the pseudo first order rate constants for the reaction of $D_n^* S$ and $D_n^* S * A_p$ with hydroxyl ion to form product carbinol, K'_{b1} and K''_{b1} are equilibrium binding constants for the two sequential steps represented in the Scheme II.1.

The binding constants K'_{b1} and K''_{b1} in Scheme II.1 may be expressed as,

$$K'_{b1} = \frac{(C_{agg1})}{(C_D)^n (C_S)} = \frac{F_m}{F_w} \cdot \frac{1}{(C_D)^n} \quad \dots (2.5)$$

$$\text{or } K''_{b1} = \frac{(C_{agg2})}{(C_{agg1}) (C_A)^p} \quad \dots (2.6)$$

where C_{agg1} and C_{agg2} correspond to molar concentrations of $D_n^* S$ and $D_n^* S * A_p$ respectively. Equations (2.3) and (2.5) may be solved to give

$$\log \frac{k_w - k_\psi}{k_\psi - k_{m1}} = \log K'_{b1} + n \log C_D \quad \dots (2.7)$$

Similarly Equations (2.3) and (2.6) may be solved to give

$$\log \frac{k_{m1} - k_\psi}{k_\psi - k_m} = \log K''_{b1} + p \log C_A \quad \dots (2.8)$$

The overall binding constant K_{b1} is given by the product of equilibrium constants K'_{b1} and K''_{b1} corresponding to Scheme II.1:

$$K_{b1} = K'_{b1} \cdot K''_{b1} \quad \dots (2.9)$$

II.3.2 Scheme II.2

The binding constant, K_{b2} , for the reaction Scheme II.2 may be written as,

$$K_{b2} = \frac{(C_{agg3})}{(C_D)^n (C_S) (C_A)^p (C_I)^q} \quad \dots (2.10)$$

$$\text{or } F_m = \frac{K_{b2} (C_D)^n (C_A)^p (C_I)^q}{1 + K_{b2} (C_D)^n (C_A)^p (C_I)^q} \quad \dots (2.11)$$

where C_{agg3} denotes molar concentration of aggregates $D_n^*S^*A_p^*I_q$.

Elimination of F_m and F_w from Equations (2.3) and (2.11) gives

$$\frac{k_m - k_\psi}{k_\psi - k_w} = \frac{1}{K_{b2} (C_D)^n (C_A)^p (C_I)^q} \quad \dots (2.12)$$

$$\text{or } \log \frac{k_\psi - k_w}{k_m - k_\psi} = \log K_{b2} + n \log C_D + p \log C_A + q \log C_I \quad \dots (2.13)$$

When other parameters affecting the reaction rate are held constant, Equation (2.13) may be utilized to give the value of n, a number analogous to cooperativity index corresponding to detergent concentration on the reaction rate. Equation (2.12) may be rearranged to give,

$$k_{\Psi} = k_m \frac{K_{b2} (C_D)^n (C_A)^p (C_I)^q}{1 + K_{b2} (C_D)^n (C_A)^p (C_I)^q} + \frac{k_w}{1 + K_{b2} (C_D)^n (C_A)^p (C_I)^q}$$

... (2.14)

Application of law of mass action to Scheme II.2b gives

$$K_e = \frac{(C_I)_m \cdot (C_A)_w}{(C_I)_w \cdot (C_A)_m} \quad \dots \quad (2.15)$$

$$\text{or } (C_I)_m = K_e \frac{(C_I)_w}{(C_A)_w} \cdot (C_A)_m \quad \dots \quad (2.16)$$

But from Equation (2.10) one may deduce,

$$(C_A)_m = p \cdot (C_S)_t \cdot F_m = p \cdot (C_S)_t \cdot \frac{K_{b2} (C_D)^n (C_A)^p (C_I)^q}{1 + K_{b2} (C_D)^n (C_A)^p (C_I)^q} \quad (2.17)$$

therefore,

$$(C_I)_m = K_e (C_S)_t \cdot p \cdot \frac{K_{b2} (C_D)^n (C_A)^p (C_I)^p}{1 + K_{b2} (C_D)^n (C_A)^p (C_I)^q} \quad \dots \quad (2.18)$$

The pseudo first order rate constant, k_m can now be written from bimolecular rate constant k' , an intrinsic micellar parameter 'f' and concentration of reactant in or on the catalytic micelles as under:

$$k_m = f \cdot k' \cdot (C_I)_m \quad \dots (2.19)$$

The intrinsic micellar parameter 'f' denotes the factor by which bimolecular rate constant k' is changed in micellar environment due to proximity effects and changes in the other thermodynamic parameters of the reaction caused by various interactions in presence of micelle-forming surfactant in the reaction system.

Combination of Equations (2.14), (2.18) and (2.19) leads to,

$$\frac{k_\psi}{k_w} = \frac{f \cdot K_e \cdot p \cdot (C_S)_t}{C_A} \cdot \frac{\left\{ \frac{K_{b2} (C_D)^n (C_A)^p (C_I)^q}{1 + K_{b2} (C_D)^n (C_A)^p (C_I)^q} \right\}^2}{\frac{1}{K_{b2} (C_D)^n (C_A)^p (C_I)^q}} \quad \dots (2.20)$$

Equation (2.17) is a general expression which is capable of explaining the effects of the concentrations of detergent, reactant and other additives. Under the conditions when reactions follow pseudo first order kinetics the effect of substrate concentration on the rate constant may not be determined due to experimental as well as theoretical constraints for the observation of such effect.

II.4 METHOD FOR ANALYSIS OF MICELLAR DATA

II.4.1 Reactions Conforming to Scheme II.1

The plot of $\log \frac{k_\psi - k_w}{k_m - k_\psi}$ vs $\log C_D$ according to Equation (2.7) gives straight line with n and $\log K'_{b1}$ as the value of

slope and intercept respectively. In this study the effect of counter ion, the concentration of which in the reaction system is low, has been assumed to be insignificant compared to the effect of detergent. Further the studies of counterion effects and subsequent analysis of the data according to Equation (2.8), i.e., plot of $\log \frac{k_m - k_\Psi}{k_\Psi - k_m}$ vs $\log C_A$, gives the values of p and $\log K''_{b1}$. From the value of $\log K'_{b1}$ and $\log K''_{b1}$ the value of overall equilibrium constant K_{b1} may be determined according to Equation (2.9).

The values of n, p and K_{b1} may be interpreted to give an insight into the processes responsible for the micellar catalysis inhibition in the reaction system. The flow chart for the analysis of micellar data on the basis of method described¹³ here is shown in Fig. II.1.

II.4.2 Reactions Conforming to Scheme II.2

The analysis of the effect of counter ions on micellar catalysis according to Equation (2.20) may be done by the application of suitably modified numerical method¹³ of least square curve fitting described below:

Under the condition when the substrate is much saturated with the detergent ($F_m \rightarrow 1$) in the reaction system, Equation (2.20) may be transformed into following form:

$$\frac{k_\Psi}{k_w} = \frac{a.p.}{(C_A)^p} + \frac{1}{b(C_A)^p} \quad \dots (2.21)$$

Fig. II.1 Flow chart for the analysis of kinetic data for micellar effects on chemical reactions conforming to scheme II.1.

SCHEME II.1



$k_w \leftarrow$ Rate constant in bulk phase
 $k_m \leftarrow$ Rate constant at maximal micellar effects in rate vs detergent concentration profile

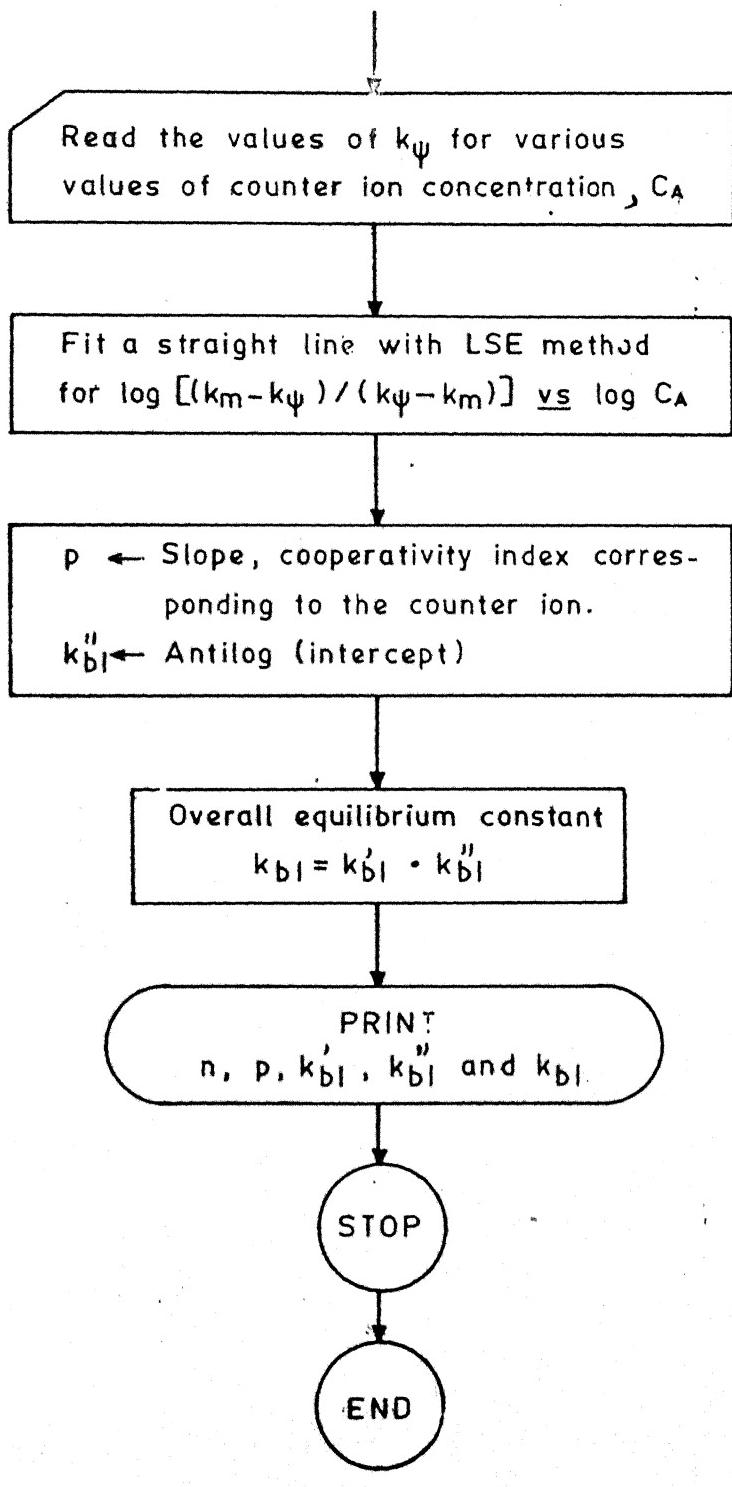
Read the values of k_ψ for various values of C_0 (k_ψ vs C_0 profile)

Fit a straight line with LSE method for $\log [(k_w - k_\psi) / (k_\psi - k_m)]$ vs $\log C_0$

$n \leftarrow$ Slope, cooperativity index corresponding to detergent
 $k_{bi}^* \leftarrow$ Antilog (intercept)

$k_m \leftarrow$ Rate const at maximal counter ion effects on overall micellar effects at constant C_0

SCHEME II.1 contd.



$$\text{where } a = K_e (C_S)_t \text{ and } b = K_{b2} (C_D)^n (C_I)^q \quad \dots (2.22)$$

Rearrangement of terms in Equation (2.22) gives,

$$\frac{k_\psi}{k_w} \cdot (C_A)^p = a \cdot (p \cdot (C_A)^{p-1}) + \frac{1}{b} \quad \dots (2.23)$$

According to Equation (2.23) the plot of derived variables $(k_\psi/k_w) \cdot (C_A)^p$ vs $p \cdot (C_A)^{p-1}$ should give straight line with 'a' and '1/b' as slope and intercept respectively, provided the correct value of p is used. The correct value of p is found out by the application of the method of successive trial. For a set of values of p the values of 'a' and '1/b' are calculated according to Equation (2.23) applying least square error method. The set of values of a and 1/b, corresponding to the values of slope and intercept respectively, for different values of p are now used to generate the plot of k_ψ vs (C_A) according to Equation (2.21). Theoretically generated plots were compared with those obtained experimentally. The value of p corresponding to theoretically calculated curve, which bears highest correlation with and has the smallest root mean square deviation from that of experimental curve, was taken to be the correct value of p. The values of 'a' and 'b' for this value of p were recorded. The value of 'a' was utilized for the calculation of f.K_e value, according to Equation (2.22), for the counterion under investigation.

Analysis of the effect of concentration of detergent according to Equation (2.13) gives the value of slope and intercept

equal to n and C_1 respectively.

$$\text{where } C_1 = \log K_{b2} + p \log C_A + q \log C_I \quad \dots \quad (2.24)$$

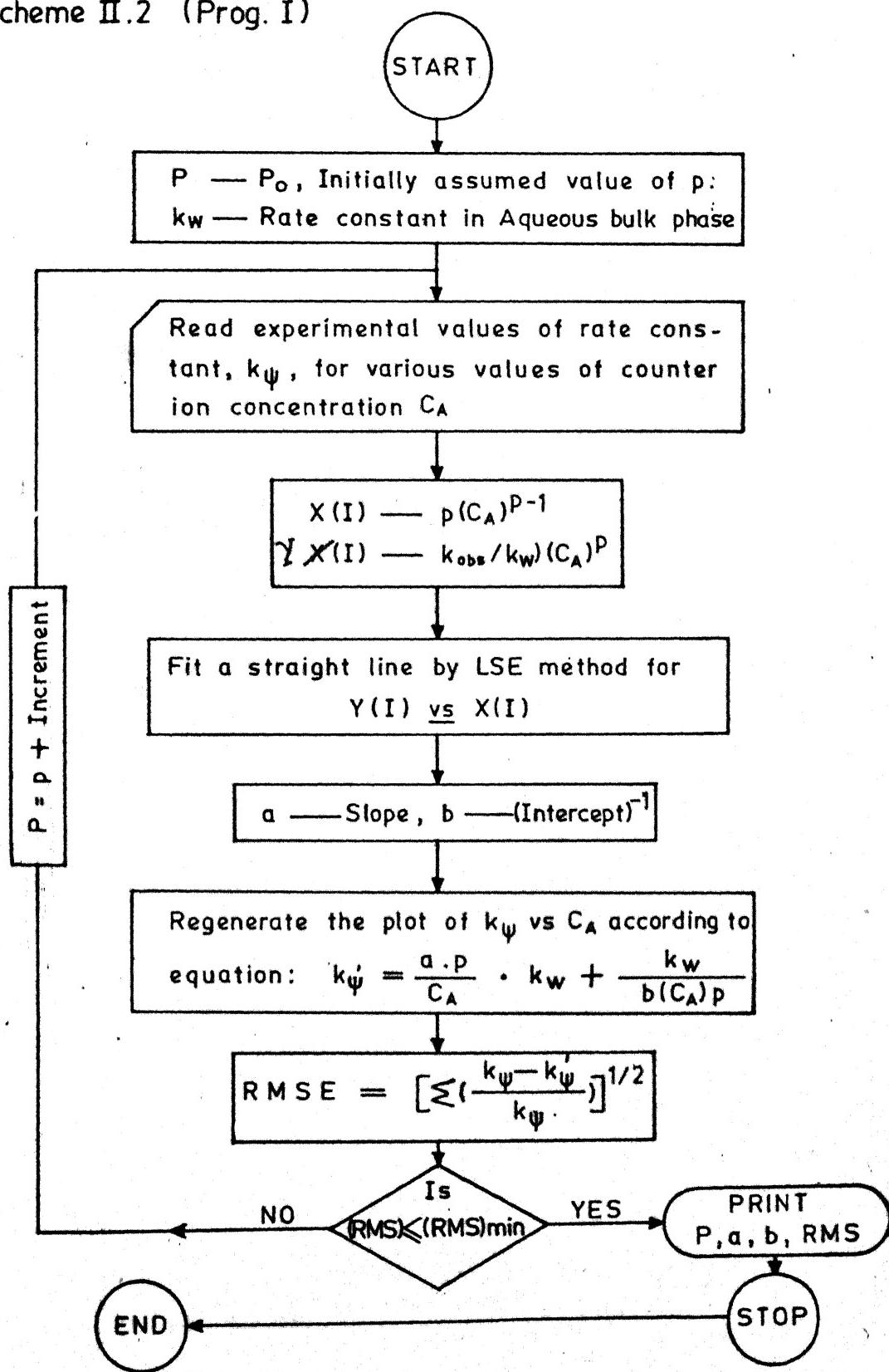
The substitution of the values of p determined earlier and the value of q which could be reasonably assumed by examining the effect of ion which is nonreactive analogue of the reactant. For example, fluoride may be taken as the nonreactive analog of hydroxyl ion for some reaction systems (see analysis data) in Equation (2.24) gives the value of equilibrium binding constant K_{b2} for the association of detergent, substrate, reactant and the counter ion originally attached to the detergent. Further the value of K_{b2} , so determined, and the relative values of b in presence of other ions, calculated according to Equation (2.23) may be utilized to calculate the values of binding constant, K_{b2} in presence of different added ions. These values of n, p and K_{b2} may be used to interpret the observed micellar effects on the chemical reactions under investigation. The flow chart for the analysis of micellar data following this method is shown in Fig. II.2.

II.5 DISCUSSION

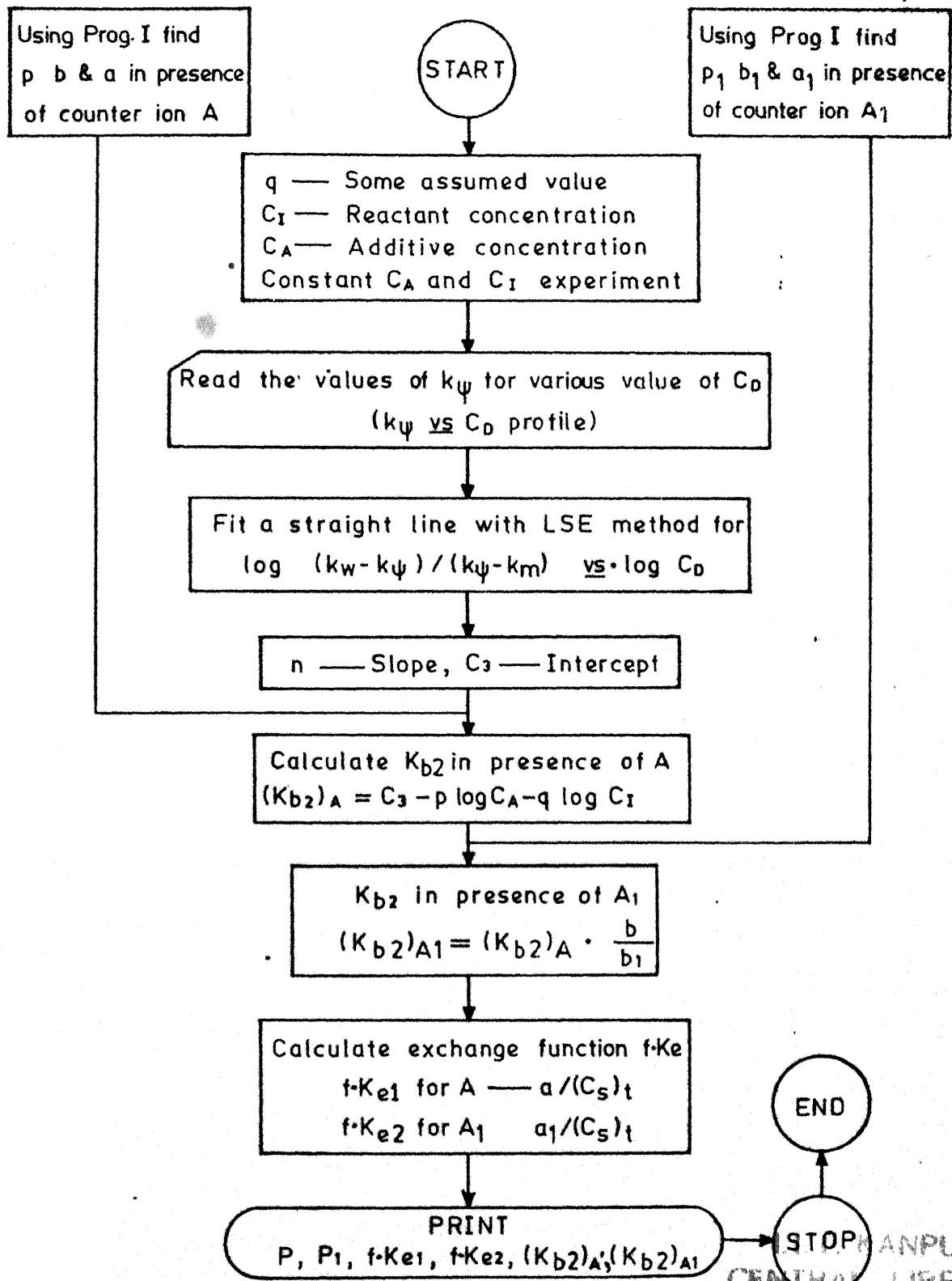
The model schemes formulated in this chapter have certain characteristic features which make it describable that micellar data for reaction kinetics in presence of micelles be analyzed and interpreted on the basis of equations derived above. The application of these equations for the analysis of micellar data does not require the predetermined value of critical micelle

Fig. II.2 Flow chart for the analysis of micellar data for the reactions conforming to scheme II.2.

Scheme II.2 (Prog. I)



(Prog. II) SCHEME II.2 (contd.)



concentration (cmc) of the surfactant. It has been pointed out that one of the necessary conditions for the reaction rates to be influenced by the presence of micelle-forming surfactants is that one or more reactants must possess hydrophobicity.¹⁶⁻²⁰ The possession of hydrophobicity by reactants in principle should alter the aggregation properties of the detergent.^{1,2} Thus the concept of critical micelle concentration under these circumstances loses its meaning. In other words the concept that only rigid micelles having a fixed number of detergent molecules, affect the reaction rate, seems inapplicable to all the systems. In this formulation less probable assumptions, such as (i) distribution of one substrate molecule per micelle; (ii) insignificant effect of substrate, electrolytes etc. on the micellar properties of the detergent and (iii) the incorporation of single counter ion may deactivate completely the micelle, have not been made.^{5,21} These model schemes describe a more realistic picture of the processes occurring in the reaction system in that it is considered that the substrate, detergent and counter ion and/or ~~and~~ participate in the formation of catalytic aggregates. However, it may be pointed out that n, p and q only represent the average numbers in which detergent, additive and reactant associate with one substrate molecule. The catalytic micelle may contain many more than one molecule each of substrate, detergent, additive and reactant species. The present treatment, of course, simplifies into one or two steps the multiple steps which must be involved in the formation of $D_n^*A_p^*S$ or $D_n^*A_p^*S^*I_q$. The validity of

this simplification is supported by the findings of Muller,²² that micellization of several detergents in nonaqueous solvents may be fit equally well by a single equilibrium model or a more complex model involving multiple steps in aggregate formation.

On the basis of these model schemes one may attempt to view the micellar reactions as models of enzymatic reactions which show positive or negative cooperativity. When applied to reactions in presence of micelle-forming surfactants these schemes allow for the evaluation of empirical parameters which may be used to explain the micellar effects. Thus this allows us to draw an analogy between micellar and enzymatic reactions on a simple mathematical basis. However, it may be pointed out that cooperativity index in micellar catalysis indicates the average number of concerned species viz., the detergent, additive or the reactant entities which on an average associate with one substrate molecule in the process of formation of catalytic aggregates whereas in enzymatic reactions positive cooperativity implies the stimulation of the interaction of the additional substrate molecule by interaction of first molecule with the enzyme. Positive cooperativity is indicated, by a value of enzymatic index of cooperativity, n , being greater than 1.0. In contrast, negative cooperativity implies the inhibition of interaction of additional molecules of the substrate by interaction of the first molecule with the enzyme. Negative cooperativity is indicated by the value of n being less than unity. In case of micellar catalysis such a distinction could not be made. For example the

detergent irrespective of the value of n , which is generally greater than 1, would catalyse or inhibit the reaction whereas the counter ions, irrespective of the value of p , which could be greater than, equal to or less than 1.0, would generally decrease the efficiency of micellar catalysis, except in a few exceptional cases.²⁴ In these model schemes it has been assumed that the overall rate of reaction is sum of the rates in complexed phase and aqueous bulk phase. The changes in the rate with increasing surfactant concentration or added salts reflect changes in the distribution of reacting species in two phases. In the derivation of equations based upon the presented model schemes it was considered that the unbound substrate reacts with reactant in the aqueous bulk phase whereas the complexes substrate reacts with the reactant in micellar phase. However, it may be made clear that the existence of other paths for the product formation may not be ruled out²⁵ viz., complexed substrate reacting with the reactant from aqueous bulk phase and vice-versa. These additional paths may also contribute to overall micellar effects and consequently to the effect of additives on micellar catalysis.

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CHAPTER III

MICELLAR EFFECT ON THE REACTION OF
TRIPHENYLMETHYL CARBONIUM IONS WITH
HYDROXYL ION: RATE VS CONCENTRATION
PROFILES FOR DETERGENTS, SUBSTRATES
AND REACTANT HYDROXYL ION.

III.1 ABSTRACT

The presence of anionic micelle-forming surfactant sodium dodecyl sulfate (SDS) inhibits whereas cationic micelle-forming surfactant cetyltrimethylammonium bromide (CTAB) catalyses the reaction of triphenylmethyl carbonium ions viz., setoglaucine (SG^+), brilliant green (BG^+) and malachite green (MG^+) with nucleophile hydroxyl ion. The plots of pseudo first order rate constant vs. detergent (CTAB or SDS) concentration for these reactions are sigmoid shaped. Variation of substrate concentration did not effect the alkaline fading reaction of these carbonium ions in presence of either SDS or CTAB showing thereby that the reactions are first order under experimental conditions. The effect of variation of hydroxyl ion concentration on these reactions in presence of SDS and CTAB was studied at concentration of the surfactants which corresponded to saturation concentration in the rate vs. detergent concentration profiles.

It is suggested that the rate vs. reactant concentration profile for reactions in presence of micelle forming surfactants, could be better understood by introducing the concept of an overall inhibition factor and an overall catalysis factor. The plot of overall inhibition factor vs. hydroxyl ion concentration for these reactions in presence of SDS gives rise to a maxima in each case suggesting the existence of optimal hydroxyl ion concentration at which maximum inhibition would be obtained. At higher hydroxyl ion concentration the plots of overall inhibition factor vs. hydroxyl ion concentration tend to overlap one another. At

optimal hydroxyl ion concentration the values of overall inhibition factor in these alkaline fading reactions are in decreasing sequence for the substrates viz., $SG^+ > BG^+ > MG^+$. When overall catalysis factor for these reactions in presence of CTAB is plotted as a function of hydroxyl ion concentration it was found that catalysis factor (CF) decreases in the beginning, then rises steeply and finally tends to attain a saturation value. Thus, for these reactions, in presence of CTAB, optimal reactant concentration may be defined as the hydroxyl ion concentration at which sufficient catalysis in the reaction rate is obtained and a further increase in the reactant concentration has only little effect on the value of overall catalysis factor. The values of overall catalysis factor at optimal hydroxyl ion concentrations vary in the order of $SG^+ > BG^+ > MG^+$. These results indicate that the substrates may be arranged in the decreasing order of their hydrophobicity as $SG > BG > MG$.

Micellar inhibition of these reactions in presence of SDS has been assigned to stabilization of ground state with respect to transition state and the non-approachability of hydroxyl ion to the carbonium ions viz., SG^+ , BG^+ and MG^+ , in the reaction systems. Catalytic effects in presence of CTAB may be attributed to the destabilization of transition state with respect to transition state and increased availability of reactant hydroxyl ion to the carbonium ions.

III.2 INTRODUCTION

Carbonium ions are known to be involved in several organic and enzymatic reactions. In view of the optimism that the knowledge of micellar catalysis may be used in organic synthesis and to explain certain biological processes, including enzyme-catalysed reactions, the understanding of mechanism and catalysis of carbonium ion reactions in presence of micelle-forming surfactants is of importance in organic chemistry and biochemistry.¹⁻⁵

When dissolved in water triphenylmethane dyes form stable carbonium ion systems in the solution. In a variety of studies these carbonium ions have been shown to react with various nucleophiles at methyl carbon atom to form covalent derivatives. The reactions are, generally, kinetically straight forward and are pseudo first order in nature.⁶⁻¹⁷ These dyes form ideal systems for the studies of micellar effects on the reactions of carbonium ions with nucleophiles.^{18,19}

The basic triphenylmethane dyes have numerous industrial, physico-chemical, biological and medicinal uses. Recently various dyes of this series have been used as analytical reagents for qualitative as well as quantitative purposes. It has been established, recently, that the efficiency of analytical determinations using these dyes could be enhanced in micellar environment.²⁰⁻²⁴ To a large extent the analytical determinations using triphenylmethane dyes are dependent upon the pH of the solution. Therefore, the studies of reaction of carbonium ions generated from triphenylmethane dyes, with nucleophiles particularly with hydroxyl ion

activation in presence of micelle forming surfactants were not reported. The effect of concentration of ionic detergents viz., cetyltrimethylammonium bromide and sodium dodecyl sulfate on this reaction has been reported by Patel and Katiyar.³⁰

The present investigations were undertaken to study the alkaline fading reaction of triphenylmethyl carbonium ion, generated from various triphenylmethane dyes viz., setoglaucine (CI basic blue 1), brilliant green (CI basic green 1) and malachite green (CI fast green 1) in presence of ionic micelle-forming surfactants viz., sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB).

In this chapter the effects of concentrations of detergents, SDS and CTAB; substrates, setoglaucine (SG^+), brilliant green (BG^+) and malachite green (MG^+) carbonium ions; and the reactant, OH^- , on micellar catalysis have been described. The nature and mechanism of micellar effects on these reactions are discussed qualitatively. The values of overall inhibition factor in presence of SDS and the values of overall catalysis factor in presence of CTAB for these reactions have been evaluated as a function of hydroxyl ion concentration over a wide range of reactant concentration.

III.3 EXPERIMENTAL SECTION

III.3.1 Reagents

Setoglaucine (rare and fine chemical) was supplied by K and K Laboratories, Inc., U.S.A., Malachite green (AnalaR) was

procured from B.D.H. England and brilliant green was obtained from E. Merck, Germany.

N-Cetyl-N,N,N-trimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) were E. Merck's guaranteed reagents.

Sodium hydroxide, oxalic acid and other salts used in this study were B.D.H. analytical grade reagents.

All these chemicals were used without any further purification.

III.3.2 Apparatus and Method

The kinetic studies were done using Beckman DU spectrophotometer. The working principle and operation of this instrument is described in its instruction manual. The change in dye cation concentration with time was followed by recording the change in the absorbance of the dye solution with respect to time at the wavelength of maximum absorbance in the reaction medium. The temperature of the cell compartment containing reaction mixture was maintained at $25 \pm 0.1^\circ\text{C}$ by circulating water in the thermo-spacer set of the spectrophotometer from an external thermostat maintained at desired temperature. The thermostat supplied by Kay Orr Bross, Calcutta, India had a temperature range of 10-100°C. The temperature was controlled by a high precision electronic relay. The room temperature was maintained in the range of $\pm 5^\circ\text{C}$ of the temperature of the thermostat. Before the start of reaction all the solutions were brought to desired temperature by keeping them for more than an hour in the thermostat. Using this

arrangement, the temperature of the solutions under investigation was kept constant within $\pm 0.1^\circ\text{C}$ of the desired value.

The pH measurements were made on an Elico pH meter model LT-10 using BDH standard buffers.

III.4 DETERMINATION OF RATE CONSTANT

For a bimolecular reaction between triphenyl carbonium ion, R^+ , and nucleophile hydroxyl ion the rate of carbinol, ROH , formation and of disappearance of reactants is given as,

$$-\frac{dc_{\text{R}^+}}{dt} = -\frac{dc_{\text{OH}^-}}{dt} = \frac{dc_{\text{ROH}}}{dt} = k' (c_{\text{OH}^-}) \cdot (c_{\text{R}^+}) \quad \dots (3.1)$$

where k' is bimolecular rate constant expressed in lit. mole $^{-1}$ sec $^{-1}$.

If the concentration of hydroxyl ion in the reaction system is in much excess to that of carbonium ion concentration, then c_{OH^-} may be regarded as constant and the reaction is first order with respect to carbonium ion, characterised by pseudo first order rate constant k , which is given by,

$$k = \frac{2.303 (\Delta \log c_{\text{R}^+})}{\Delta t} \text{ sec}^{-1} \quad \dots (3.2)$$

The real bimolecular rate constant k' may be expressed as

$$k' = k/c_{\text{OH}^-} \text{ lit. mole}^{-1} \text{ sec}^{-1} \quad \dots (3.3)$$

Generally, the reaction between triphenylmethyl carbonium ions

and nucleophiles could be followed at low concentration of the substrates because of very high value of extinction coefficients of the dyes. This makes it possible to approach ideal reaction condition needed for pseudo first order kinetics in actual practice i.e., $C_{OH} \rightarrow C_R^+$ and under this condition the alkaline fading reaction of triphenylmethyl carbonium ions goes to completion. Further, to avoid any complications due to backward reaction, arising because of the reversible nature of alkaline fading reaction of triphenylmethane dyes in general, the kinetic data may be recorded in the first few minutes of the reaction. In the present studies concerning the reaction of SG^+ , BG^+ and MG^+ carbonium ions with hydroxyl ion the interference due to backward reaction was insignificant.

In Equation (3.2) the interference due to the backward reaction was neglected and no consideration was given for the interaction of dye cation with carbinol or with water molecules. It has been observed that these effects at the experimental concentrations of carbocation and hydroxyl ion are insignificant and could be neglected.¹⁰ Sinha and Katiyar³¹ have derived a similar equation for the alkaline fading of dye cation;

$$k = k_1 + k_2 [\text{OH}] \quad \dots (3.4)$$

The expression (3.4) was derived by considering all equilibrium steps and then simplifying it on the basis of experimental conditions.

III.5 RESULTS

III.5.1 Spectra

The basic triphenylmethane dyes exhibit an intense band in visible range of the range of spectrum. The absorption spectra of substrates viz., SG, BG and MG were recorded in absence of surfactants, in presence of 0.02 M CTAB and 0.01 M SDS solutions in aqueous media. The absorption maxima for SG, BG and MG correspond to 635 nm ($\epsilon = 7.0 \times 10^4$), 620 nm ($\epsilon = 4.78 \times 10^4$) and 627.5 nm ($\epsilon = 6.2 \times 10^4$) respectively. These maxima were red shifted to 640 nm ($\epsilon = 8.4 \times 10^4$), 625 nm ($\epsilon = 5.39 \times 10^4$) and 635 nm ($\epsilon = 6.3 \times 10^4$) respectively in presence of 0.02 M CTAB solution and to 640 nm ($\epsilon = 9.0 \times 10^4$), 630 nm ($\epsilon = 7.8 \times 10^4$) and 637.5 nm ($\epsilon = 7.2 \times 10^4$) respectively in presence of 0.01 M SDS solution. The shift in the absorption maxima of the dyes in micellar environment is indicative of binding of substrate with the micelle-forming surfactant.¹⁴

Nonapplicability of Beer's law to the triphenylmethane dyes has been reported in the literature.¹⁵ The applicability of Beer's law was examined for each of the dyes in absence as well as in presence of detergent solutions viz., 0.01 M SDS and 0.02 M CTAB. It was found that dyes obey Beer's law at lower concentrations, i.e., upto 2×10^{-5} M. The reactions of these dyes with hydroxyl ion were, therefore, studied at concentration of the substrate either lower than or in the vicinity of 2.0×10^{-5} M.

III.5.2 THE ALKALINE FADING REACTION OF TRIPHENYLMETHYL CARBONIUM IONS IN PRESENCE OF SODIUM DODECYL SULFATE

III.5.2.1 Effect of SDS Concentration on Reaction Rate

The effect of concentration of SDS, an anionic micelle-forming surfactant, on the reaction rate was studied at fixed concentrations of the substrate, reactant and the counter ion attached to detergent. The counter ion concentration was maintained constant by adding necessary amount of it in the reaction system from a stock solution.

a. Reaction of SG⁺ carbonium ion with hydroxyl ion: The fading reaction of SG⁺ carbonium ion with hydroxyl ion at low hydroxyl ion concentration, at which measurable reaction rate in absence of SDS is observed, is inhibited almost completely when SDS is added in the reaction system. This makes it difficult to study the effect of SDS in a wider range of concentration of the detergent, particularly at higher surfactant concentrations. Also, if the concentration of hydroxyl ion in the reaction system is increased (>0.1 M) the reaction becomes fast and thus the determination of rate constant in the absence of surfactant becomes difficult. The reaction was, therefore, studied at two different concentrations of hydroxyl ion viz., at 0.1 M and at 0.5 M. At these concentrations of reactant, measurable rates were observed in presence of SDS over a wider range of SDS concentration. The results are summarised in Table III.1. The values of pseudo first order rate constant in absence of SDS at 0.1 M and 0.5 M hydroxyl ion concentrations were obtained by extrapolation of the

Table III.1. Variation of pseudo first order rate constant, k_{ψ} , for the reaction of SG⁺ carbonium ion with hydroxyl ion as a function of SDS concentration at 25°C

Sl. No.	[SDS]	First Order Rate Constant $k_{\psi} \times 10^2 \text{ min}^{-1}$	
		[SG ⁺] = $1.2 \times 10^{-5} \text{ M}$	[SG ⁺] = $1.6 \times 10^{-5} \text{ M}$
		[OH ⁻] = 0.1 M	[OH ⁻] = 0.5 M
1.	0.00000	32.61	171.00
2.	0.00002	32.61	
3.	0.00004	31.66	
4.	0.00006	31.66	
5.	0.00008	31.75	
6.	0.00010	29.84	
7.	0.00016	27.41	
8.	0.00020	25.61	29.00
9.	0.00024	21.10	
10.	0.00030	14.10	16.243
11.	0.00036	9.023	
12.	0.00040	5.701	5.820
13.	0.00048	3.786	
14.	0.00054	3.825	
15.	0.00070	1.267	
16.	0.00080	0.9285	4.477
17.	0.0010	0.532	4.524
18.	0.0015	0.357	
19.	0.0020	0.346	3.914
20.	0.0030	0.321	
21.	0.0040		3.972
22.	0.0050	0.321	
23.	0.0060		3.972
24.	0.0070		3.972
25.	0.0080	0.318	3.914
26.	0.0090		3.972
27.	0.010	0.321	3.972

linear plot of rate constant vs hydroxyl ion concentration in aqueous media. Figure III.1 exhibits the detergent SDS, concentration vs rate profile for this reaction.

b. Reaction of BG^+ carbonium ion with hydroxyl ion: The effect of SDS concentration on the reaction of BG^+ carbonium ion was studied by keeping concentrations of substrate (1.0×10^{-5} M), hydroxyl ion (0.01 M) and the counter ion i.e., Na^+ (0.02 M) constant. The values of pseudo first order rate constant, k_p , as a function of varying SDS concentration are recorded in Table III.2.

c. Reaction of MG^+ carbonium ion with hydroxyl ion: The effect of SDS concentration on the reaction of MG^+ carbonium ion with hydroxyl ion was studied at fixed concentrations of MG^+ (1.1×10^{-5} M), hydroxyl ion (0.005 M) and counter ion sodium (0.015 M) and varying concentration of SDS in the reaction system. The values of pseudo first order rate constant for this reaction as a function of varying SDS concentration are summarised in Table III.2.

d. General features of rate vs surfactant profile: It may be noted from Tables III.1 and III.2 and Fig. III.1 that for the reaction of triphenylmethyl carbonium ions viz., SG^+ , BG^+ and MG^+ with hydroxyl ion in presence of SDS the inhibition is not only exhibited but also attains saturation well below the critical micelle concentration¹ (CMC) of pure SDS in aqueous medium which is 0.008 M. This phenomenon indicates the existence of catalytically functional (pre)micellar aggregates in the reaction

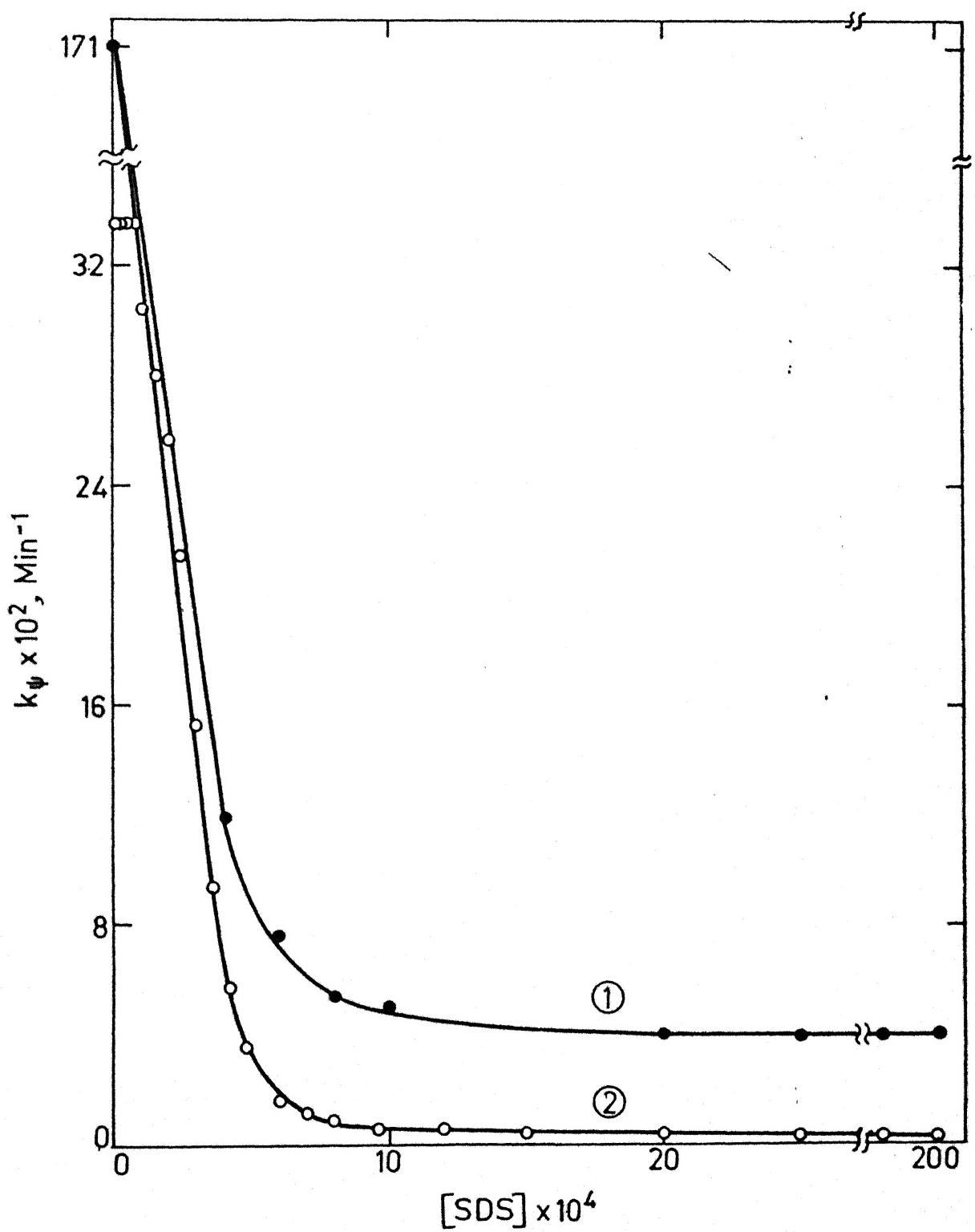


Fig. III.1 Pseudo first order rate constant for the fading reaction of SG^+ carbonium ion in presence of (1) 0.1M and (2) 0.5 NaOH plotted as a function of SDS concentration at 25°C.

Table III.2. Variation of pseudo first order rate constant, k_ψ , for the reaction of BG^+ and MG^+ carbonium ion with hydroxyl ion as a function of SDS concentration at 25°C.

Sl. No.	[SDS]	First Order Rate Constant $k_\psi \times 10^2 \text{ min}^{-1}$	
		$[BG^+] = 1.0 \times 10^{-5} \text{ M}$	$[MG^+] = 1.1 \times 10^{-5} \text{ M}$
		$[OH^-] = 0.01 \text{ M}$	$[OH^-] = 0.005 \text{ M}$
1.	0.00000	37.56	56.27
2.	0.00001	37.56	55.27
3.	0.00003	37.56	55.27
4.	0.00004	32.70	
5.	0.00006	25.97	55.27
6.	0.00008	25.37	52.10
7.	0.00012	18.57	49.51
8.	0.00016	14.93	
9.	0.00020	12.15	
10.	0.00024	11.71	
11.	0.00036	7.99	43.20
12.	0.0004	5.93	
13.	0.0005	5.60	
14.	0.00052		40.59
15.	0.00056		38.30
16.	0.00060	5.247	36.56
17.	0.00064		32.81
18.	0.00070	4.204	
19.	0.00072		28.21
20.	0.00080	3.16	23.32
21.	0.00088		22.17
22.	0.00090	2.58	
23.	0.0010	2.23	18.99
24.	0.0014		12.42
25.	0.002	1.94	3.858
26.	0.003		1.407
27.	0.005	0.661	0.852
28.	0.010	0.660	0.852

system. Further, the values of factor of overall inhibition in presence of 0.1 M and in 0.5 M hydroxyl ion for the alkaline fading reaction of SG^+ carbonium ion are 101.6 and 45.7. This demonstrates that the factor of inhibition in presence of SDS for this type of reactions changes with the alteration of hydroxyl ion concentration in the reaction system.

III.5.2.2 Effect of Substrate Concentration of Reaction Rate

The dependence of the pseudo first order rate constant on the substrate concentration was studied by keeping the concentrations of SDS and hydroxyl ion constant and varying the concentration of the substrate i.e., carbonium ion in the reaction system. The alkali concentration was taken in large excess with respect to dye concentration to avoid the influence of backward reaction. The kinetic data for rate vs substrate concentration profile for these reactions in presence of SDS are shown in Fig. III.2.

a. Reaction of SG^+ carbonium ion : The effect of SG^+ concentration of the reaction rate was studied by varying SG^+ concentration from 6×10^{-6} M to 1.2×10^{-5} M at fixed concentrations of SDS (0.01 M) and hydroxyl ion (0.1 M). The values of first order rate constant, k_{H} , are summarised in Table III.3.

b. Reaction of BG^+ carbonium ion : The effect of substrate concentration on the reaction of BG^+ carbonium ion with hydroxyl was examined at fixed concentrations of SDS (0.01 M) and hydroxyl ion (0.10 M) in the range of BG^+ concentration varying from 8.0×10^{-6} M

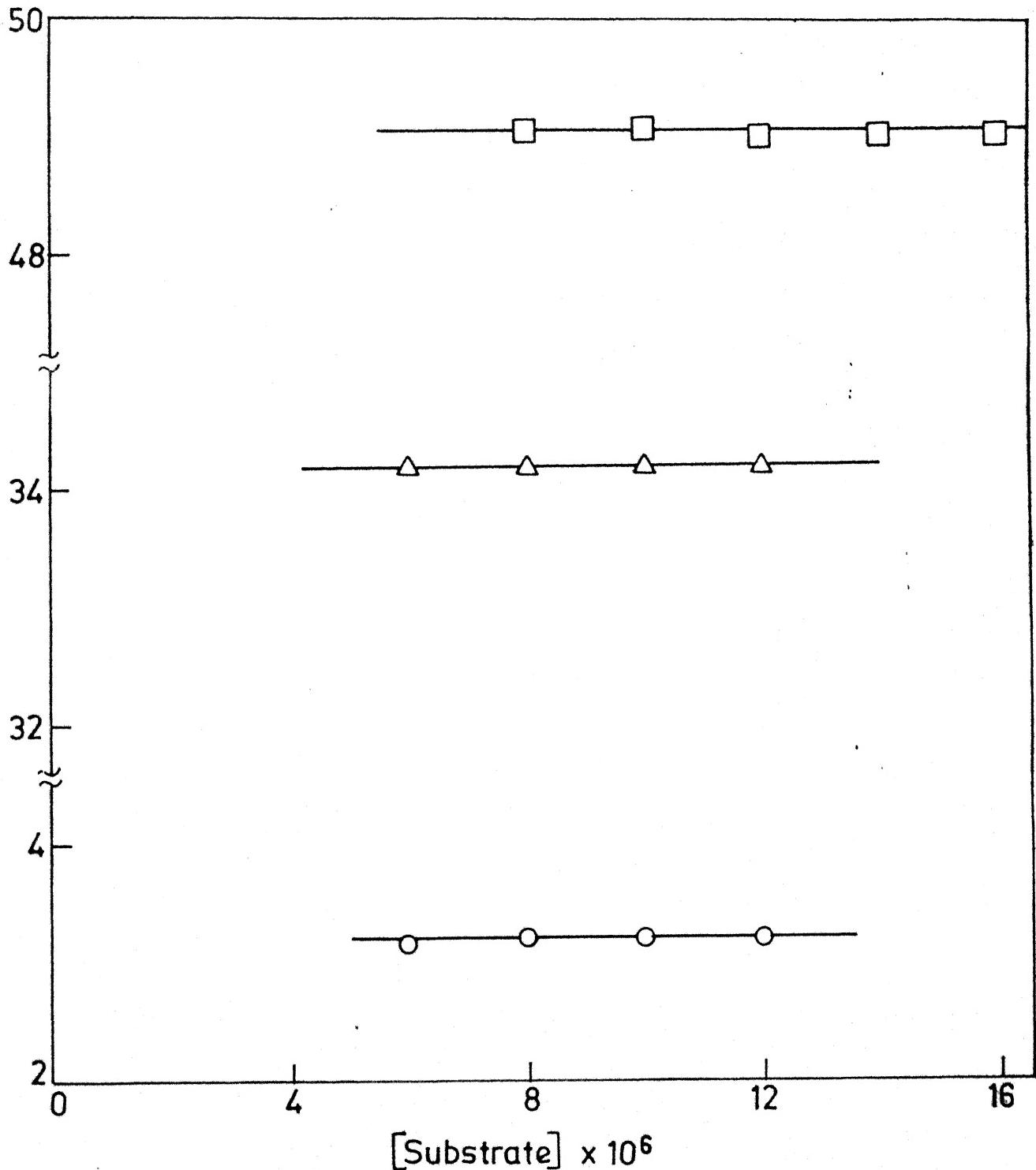


Fig. III.2 Effect of substrate concentration on the alkaline fading reaction of SG⁺(○), MG⁺(△) and BG⁺(□) carbonium ions in presence of 0.01M SDS in aqueous media at 25°C.

Table III.3. Variation of pseudo first order rate constant, k_{ψ} , for the reaction of triphenylmethyl carbonium ions with hydroxyl ion as a function of substrate concentration in presence of SDS at 25°C.

Sl.No.	Substrate Concentration (in mole/litre)	First Order Rate Constant, $k_{\psi} \times 10^3 \text{ min}^{-1}$
<u>I. Reaction of SG⁺ carbonium ion with hydroxyl ion:</u>		
	$[\text{SDS}] = 0.01 \text{ M}; [\text{OH}^-] = 0.10 \text{ M}$	
1.	0.6×10^{-5}	3.18
2.	0.8×10^{-5}	3.21
3.	1.0×10^{-5}	3.18
4.	1.2×10^{-5}	3.21
<u>II. Reaction of BG⁺ carbonium ion with hydroxyl ion:</u>		
	$[\text{SDS}] = 0.01 \text{ M}; [\text{OH}^-] = 0.10 \text{ M}$	
1.	0.8×10^{-5}	49.05
2.	1.0×10^{-5}	49.11
3.	1.2×10^{-5}	49.02
4.	1.4×10^{-5}	49.05
<u>III. Reaction of MG⁺ carbonium ion with hydroxyl ion:</u>		
	$[\text{SDS}] = 0.01 \text{ M}; [\text{OH}^-] = 0.05 \text{ M}$	
1.	0.6×10^{-5}	34.20
2.	0.8×10^{-5}	34.25
3.	1.0×10^{-5}	34.20
4.	1.2×10^{-5}	34.20

to 1.4×10^{-5} M. The values of pseudo first order rate constant as a function of dye concentration are recorded in Table III.3.

c. Reaction of MG⁺ carbonium ion: Similar studies were done in case of the reaction of MG⁺ carbonium ion with hydroxyl ion at constant concentrations of SDS (0.01 M) and hydroxyl ion (0.05 M) in the concentration range of MG⁺ varying from 0.6×10^{-5} M to 1.2×10^{-5} M. The kinetic data are summarised in Table III.3.

d. General features of rate vs substrate concentration profile: It may be noted from the data summarised in Table III.3 and Fig. III.2 that the value of pseudo first order rate constant, k_f, in micellar environment of SDS is independent of initial substrate concentration in the reaction system. This indicates that the reactions of triphenylmethyl carbonium ions with hydroxyl ion under investigation are bimolecular but first order in nature under the condition of excess of alkali in the reaction systems.

III.5.2.3 Effect of Nucleophile Concentration on Reaction Rate

The effect of reactant concentration on the pseudo first order rate constant was studied in presence of constant concentrations of SDS, substrate and by varying the hydroxyl ion concentration in the reaction system.

a. Reaction between SG⁺ carbonium ion and hydroxyl ion: The effect of variation of hydroxyl ion concentration on the reaction rate was studied in presence of fixed concentrations of SDS (0.01 M) and SG⁺ (0.8×10^{-6} M) by varying hydroxyl ion concentration in

the reaction system. The values of pseudo first order rate constant for the effect of variation of reactant concentration in the range of 0.10 M to 0.50 M are summarized in Table III.4.

b. Reaction between BG^+ carbonium ion and hydroxyl ion: The effect of hydroxyl ion concentration on the pseudo first order rate constant was examined at fixed concentrations of detergent (0.01 M) and the substrate (1.0×10^{-5} M) by varying reactant concentration in the range of 0.01 M to 0.30 M. The kinetic data for this reaction are summarized in Table III.4 and also shown in Fig. III.3.

c. Reaction between MG^+ carbonium ion and hydroxyl ion: The effect of reactant concentration of pseudo first order rate constant for the reaction of MG^+ carbonium ion with hydroxyl ion was studied by keeping the concentrations of SDS (0.01 M) and MG^+ (1.1×10^{-5} M) fixed and varying hydroxyl ion concentration from 0.005 M to 0.20 M in the reaction system. The values of first order rate constant are shown in Table III.4 and Fig. III.3.

d. General features of rate vs reactant concentration profile: It may be noted from Table III.4 and Fig. III.3 that on the SDS inhibited reaction of SG^+ , BG^+ and MG^+ carbonium ions with hydroxyl ion, the increase in the hydroxyl ion concentration in reaction system has the effect of increasing the value of pseudo first order rate constant. The trend in variation of rate constant k_4 vs hydroxyl ion concentrations can be understood by considering the factor of overall inhibition for the reaction at given by

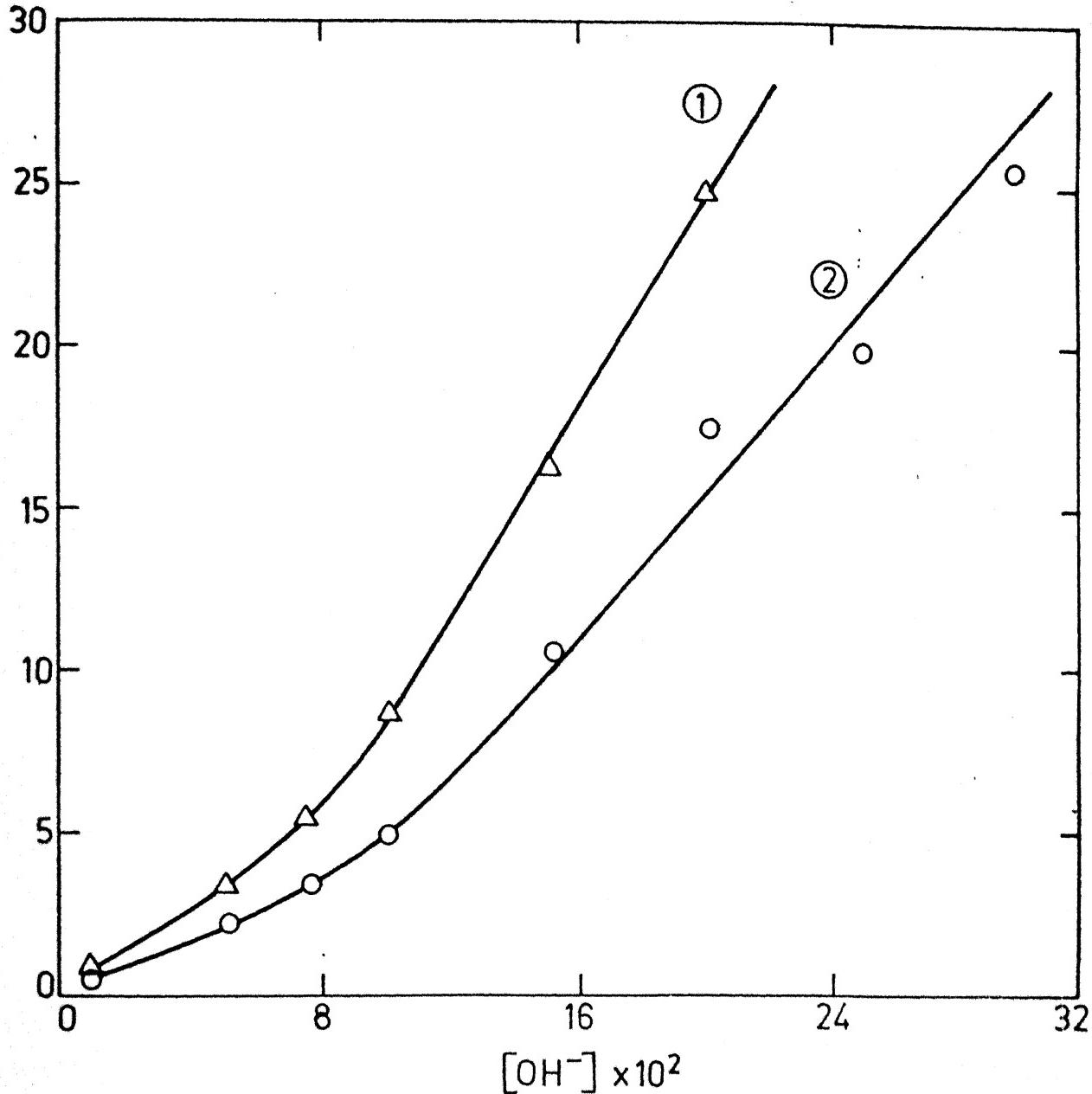


Fig. III.3 Rate vs hydroxyl ion concentration profile for the alkalines fading reaction of MG⁺(Δ) and BG⁺(\circ) carbonium ions in presence of SDS at 25° C.

Table III.4. The values of pseudo first order rate constant, k_{ψ} , in presence of 0.01 M SDS as a function of hydroxyl ion concentration for the alkaline fading reaction of triphenylmethyl carbonium ions at 25°C

Sl. No.	$[\text{OH}^-] \times 10^2$	Rate Constant $k_{\psi} \times 10^2 \text{ min}^{-1}$		
		$[\text{SG}^+] = 0.8 \times 10^{-5} \text{ M}$	$[\text{BG}^+] = 1.0 \times 10^{-5} \text{ M}$	$[\text{MG}^+] = 1.1 \times 10^{-5} \text{ M}$
1.	1.0		0.66	1.01
2.	5.0		2.23	3.43
3.	7.5		3.42	5.37
4.	10.0	0.321	4.91	8.65
5.	15.0		10.58	16.22
6.	20.0	1.073	17.46	24.83
7.	25.0			
8.	30.0	2.111	25.52	
9.	40.	3.186		
10.	50.0	4.52		

Table III.5. The variation of overall inhibition factor as a function of hydroxyl ion concentration in presence of 0.01 M SDS at 25°C.

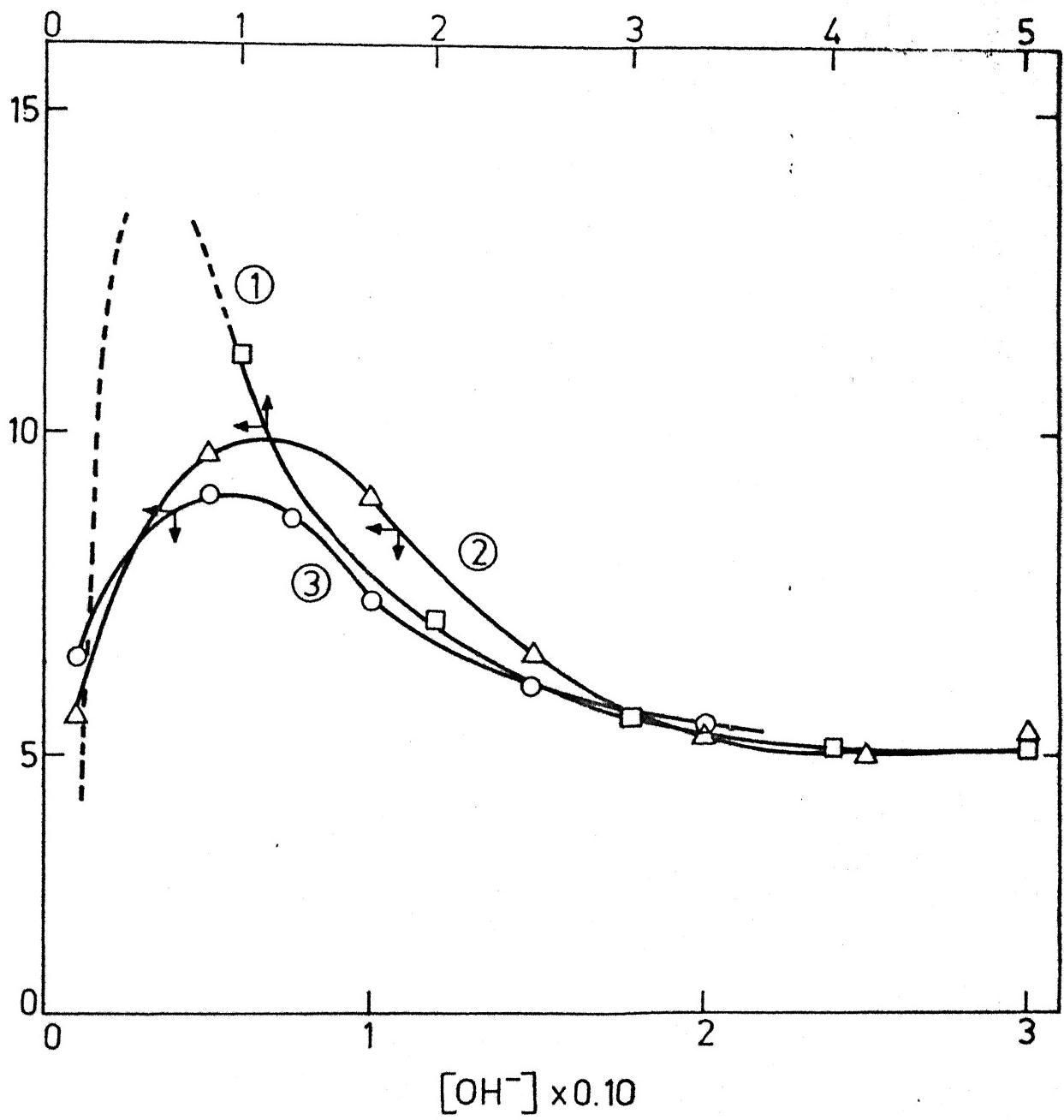
Sl.No.	$[\text{OH}^-] \times 10^2$	Overall Inhibition Factor for the Alkaline Fading Reaction of		
		SG^+ ion	BG^+ ion	MG^+ ion
1.	1.00		56.42	64.81
2.	5.00		88.79	80.56
3.	7.50		87.11	77.16
4.	10.00	101.56	80.65	83.89
5.	15.00		55.97	51.11
6.	20.00	60.78	43.24	45.50
7.	25.00		40.83	
8.	30.00	46.34		
9.	40.00	40.94		
10.	50.00	40.76		

hydroxyl ion concentration, which may be expressed as,

$$\text{Inhibition Factor, I.F.} = \left(\frac{k_w}{k_\psi} \right) [\text{OH}^-] = \text{constant} \quad \dots \quad (3.5)$$

where k_w is reaction rate constant at some hydroxyl ion concentration in the reaction system and k_ψ is the value of observed pseudo first order rate constant at same hydroxyl ion concentration in presence of SDS.

It may be noted from Table III.5 that at very low hydroxyl ion concentration the factor of inhibition is very small for the reaction of MG^+ and BG^+ carbonium ion reactions. This factor for the reaction of SG^+ ion could not be evaluated due to very slow nature of the reaction at such low hydroxyl ion concentrations. At increased hydroxyl ion concentration the factor of inhibition has higher value but this decreases as a function of further increase in hydroxyl ion concentration. Thus, only in a narrow concentration range of hydroxyl ion, the variation of rate constant vs reactant concentration may be regarded as linear as exhibited in the Fig. III.4. The value of inhibition factor in lower hydroxyl ion concentration range increases steeply with increasing $[\text{OH}^-]$, attains a maxima and then starts decreasing afterwards. Figure III.4 shows that there is an optimal hydroxyl ion concentration at which maximum inhibition in the reaction of triphenylmethyl carbonium ion with hydroxyl is obtained. This observation of micellar catalytic effect is similar to the behaviour of enzymes in as much as the activity of enzymes is known to



III.4 Variation of overall inhibition factor as a function of hydroxyl ion concentration in presence of SDS for the alkalins fading reaction of SG⁺(□), BG⁺(△) and MG⁺(○) carbonium ions at 25°C.

be highest at some optimal pH and substrate concentration.²⁷

III.5.3 THE ALKALINE FADING REACTION OF TRIPHENYL CARBONIUM IONS IN PRESENCE OF CETYLTRIMETHYLMONIUM BROMIDE

III.5.3.1 Effect of CTAB Concentration on Reaction Rate

The effect of variation of CTAB concentration, a cationic micelle-forming surfactant, on reaction rate of carbonium ions viz., SG⁺, BG⁺ and MG⁺ with hydroxyl ion was investigated at fixed concentrations of substrate, reactant (i.e., hydroxyl ion) and the counter ion (bromide ion). The counter ion concentration was maintained constant by adding necessary amount of potassium bromide in the reaction system from a stock solution.

a. Reaction of SG⁺ carbonium ion with hydroxyl ion: The effect of CTAB on the alkaline fading reaction of SG⁺ carbonium ion was studied at fixed concentrations of substrate (1.5×10^{-5} M), reactant (0.01 M) and the counter ion i.e., bromide (0.02 M). The values of pseudo first order rate constant as a function of varying CTAB concentration are summarised in Table III.6. The effect of CTAB on the reaction rate is exhibited in Fig. III.5. It may be observed that the reaction rate remains invariant in the initial stage and then increases steeply reaching a final saturation value with increasing CTAB concentration in the reaction system.

b. Reaction of BG⁺ carbonium ion with hydroxyl ion: The effect of detergent concentration on the pseudo first order rate constant for the reaction of BG⁺ carbonium ion with hydroxyl ion was

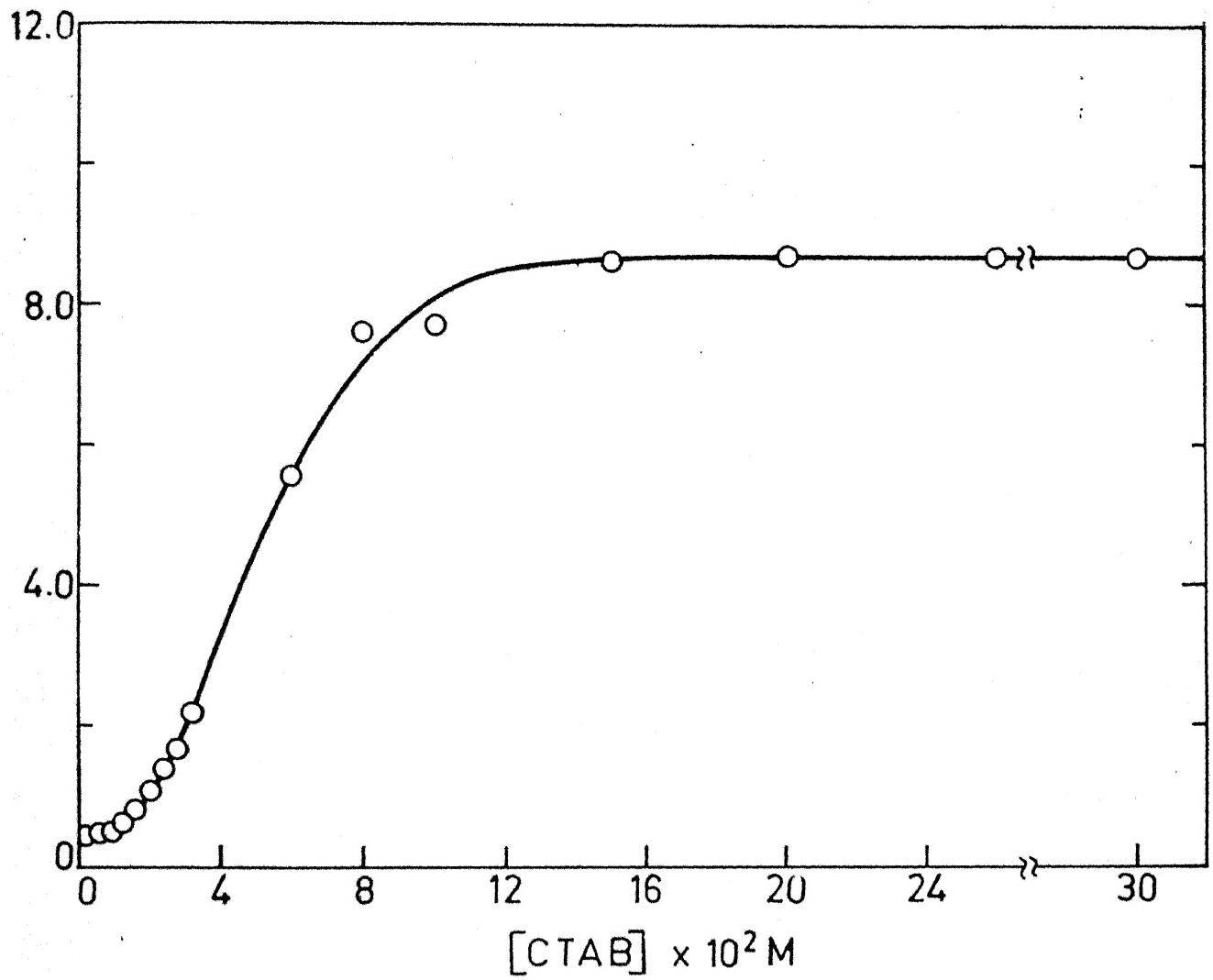


Fig. III.5 First order rate constant for CTAB catalysed reaction of SG^+ carbonium ion with hydroxyl ion as a function of detergent concentration at 25° C.

Table III.6. Variation of pseudo first order rate constant, k_{ψ} , as a function of CTAB concentration for the reaction of various triphenylmethyl carbonium ions with hydroxyl ion at 25°C

Sl. No.	[CTAB]	$k_{\psi} \times 10^2 \text{ min}^{-1}$		
		$[\text{SG}^+] = 1.5 \times 10^{-5} \text{ M}$ $[\text{OH}^-] = 0.01 \text{ M}$	$[\text{BG}^+] = 1.6 \times 10^{-5} \text{ M}$ $[\text{OH}^-] = 9.25 \text{ M}$	$[\text{MG}^+] = 1.8 \times 10^{-5} \text{ M}$ $[\text{OH}^-] = 0.001 \text{ M}$
1.	0.0000	4.613	0.461	9.605
2.	0.0001	4.615	0.461	
3.	0.0003	4.613		
4.	0.0004	4.617	2.315	9.636
5.	0.0005	4.617		
6.	0.0006	4.613	3.380	9.625
7.	0.0008	4.630	4.307	4.327
8.	0.0010		4.998	14.85
9.	0.0012	5.758		
10.	0.0015			15.20
11.	0.0016	8.636		
12.	0.0020	11.23	7.517	18.20
13.	0.0024	13.82		
14.	0.0028	17.13		
15.	0.0030		8.911	33.39
16.	0.0032	22.17		
17.	0.0040	57.00	8.955	40.11
18.	0.0050			46.06
19.	0.0060	55.27	8.955	52.01
20.	0.0070			55.96
21.	0.0080	76.46	9.185	60.84
22.	0.0100	77.15	9.220	89.82
23.	0.0140		8.955	
24.	0.0150	85.89		89.92
25.	0.0180		8.816	
26.	0.0200	85.78	8.955	89.7
27.	0.0250			90.39

studied in presence of potassium dihydrogenphosphate hydroxyl ion buffer at pH of the reaction system, maintained constant (9.25). This buffer has been reported to have insignificant effect on micellar catalysis of reactions involving acid or base hydrolysis since introduction of micelle-forming surfactant in this buffer has no effect on the organization $[H^+]$ or $[OH^-]$ in the solution, and thus pH in aqueous bulk phase as well as in complexed micellar phase may be assumed to be the same.²⁰ The concentrations of substrate (1.6×10^{-5} M) and the counter ion (0.02 M) were also maintained constant. The values of pseudo first order rate constant with varying CTAB concentration are recorded in Table III.6. The behaviour that the reaction rate remains unperturbed in the beginning then rises steeply attaining a final saturation with increasing CTAB concentration is evident from the kinetic data.

c. Reaction of Mg^+ carbonium ion with hydroxyl ion: The values of pseudo first order rate constant for the reaction of Mg^+ carbonium ion with hydroxyl ion were determined at fixed concentrations of substrate (1.8×10^{-5} M) hydroxyl ion (0.001 M) and the bromide ion (0.02 M) as a function of varying CTAB concentration. The kinetic data are summarised in Table III.6. It may be noted that the rate of reaction upto 0.0002 M CTAB concentration remains invariant and afterwards rises steeply resulting finally in a saturation value with increasing CTAB concentration.

d. General features of rate vs detergent concentration profile:

It may be noted from Fig. III.5 as well as from Table III.6 that

the value of pseudo first order rate constant at low concentrations of CTAB in the beginning remains constant. As the CTAB concentration is further increased the value of rate constant, increases steeply resulting finally in a saturation value with the increasing detergent concentration. The observation of catalysis below CMC in case of BG^+ , MG^+ indicates that catalytically functional (pre)micellar aggregates are formed in the reaction systems.

III.5.3.2 Effect of Substrate Concentration on the Reaction Rate

The dependence of reaction rate on the substrate concentration in presence of CTAB was studied by recording pseudo first order rate constant, k_ψ , at fixed concentrations of the reactant and the detergent and varying the substrates viz., SG^+ , BG^+ and MG^+ concentration in the reaction system. The concentration of hydroxyl ion in the reaction was maintained such that interference due to backward reactions on the studies would be insignificant. Table III.7 and Fig. III.6 summarize the effect of substrate concentration, viz., SG^+ , BG^+ and MG^+ on the alkaline fading reactions of the dyes cations in presence of CTAB.

a. Alkaline fading reaction of SG^+ carbonium ion: The effect of SG^+ carbonium ion concentration on the rate of alkaline fading reaction was studied by keeping the concentrations of CTAB (0.02M) and the reactant hydroxyl ion (0.01 M) fixed and varying substrate concentration in the range 1.4×10^{-5} M to 2.0×10^{-5} M.

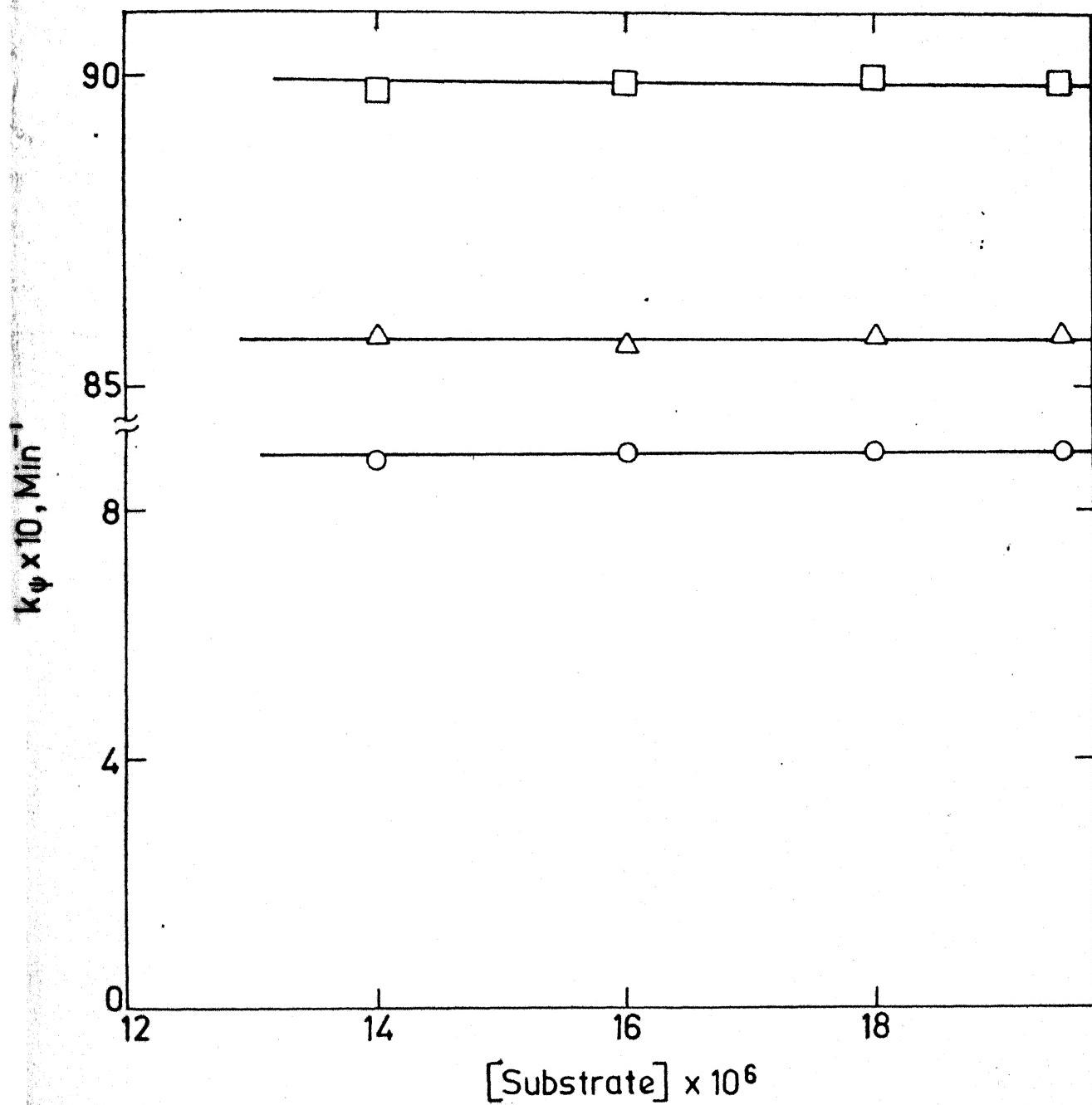


Fig. III.6. The effect of substrate concentration on the reaction of SG⁺ (Δ), BG⁺ (\circ) and MG⁺ (\square) carbonium ions with hydroxyl ion in presence of 0.02 M aqueous CTAB solution at 25°C.

Table III.7. Variation of rate constant, k_{ψ} , with substrate concentration in presence of 0.02 M CTAB for the reactions of various triphenylmethyl carbonium ions at 25°C.

Sl.No.	Substrate Concentration (in mole/litre)	First Order Rate Constant $k_{\psi} \times 10^2 \text{ min}^{-1}$
--------	--	--

I. Reaction of SG⁺ carbonium ion with hydroxyl ion:

$$[\text{OH}^-] = 0.01 \text{ M}$$

1.	1.4×10^{-5}	85.78
2.	1.6×10^{-5}	85.56
3.	1.8×10^{-5}	85.78
4.	2.0×10^{-5}	85.78

II. Reaction of BG⁺ carbonium ion with hydroxyl ion:

$$\text{pH} = 9.25$$

1.	1.4×10^{-5}	8.816
2.	1.6×10^{-5}	8.955
3.	1.8×10^{-5}	8.955
4.	2.0×10^{-5}	8.955

III. Reaction of MG⁺ carbonium ion with hydroxyl ion:

$$[\text{OH}^-] = 0.001 \text{ M}$$

1.	1.4×10^{-5}	89.74
2.	1.6×10^{-5}	89.91
3.	1.8×10^{-5}	90.39
4.	2.0×10^{-5}	89.91

b. Alkaline fading reaction of BG^+ carbonium ion: The effect of substrate concentration on the reaction of BG^+ carbonium ion with hydroxyl ion was examined at fixed concentration of CTAB (0.02 M) and pH 9.25. The pH of the reaction system was maintained by using potassium dihydrogen orthophosphate-sodium hydroxide buffer. The BG^+ concentration was varied in the range 1.4×10^{-5} M to 2.0×10^{-5} M.

c. Alkaline fading reaction of MG^+ carbonium ion: The effect on the reaction rate constant as a function of substrate concentration for the alkaline fading reaction of MG^+ carbonium ion was studied in presence of fixed concentrations of CTAB (0.02 M) and hydroxyl ion (0.001 M) in the reaction system. The substrate concentration was varied from 1.4×10^{-5} M to 2.0×10^{-5} M.

d. General features of rate vs substrate concentration profile:
 It may be noted from the data summarized in Table III.7 as well as in Fig. III.6 that the values of pseudo first order rate constant, k_p , are independent of initial substrate concentration in the reaction system for all the carbonium ions viz., SG^+ , BG^+ and MG^+ . These studies demonstrate the reaction of carbonium ions, generated from triphenylmethane dyes, with hydroxyl ion are bi-molecular in nature but follow first order kinetics under the condition of excess of reactant concentration in the reaction system.

III.5.3.3 Effect of Nucleophile Concentration on Reaction Rate

The effect of reactant hydroxyl ion concentration on the alkaline fading reaction of SG^+ , BG^+ and MG^+ carbonium ions in

presence of CTAB was investigated by keeping the concentrations of substrate and the detergent fixed and varying the concentration of hydroxyl ion in the reaction system.

a. Reaction between SG⁺ and hydroxyl ion: For this reaction the effect of variation of hydroxyl ion concentration on the pseudo first order rate constant was examined in presence of fixed concentrations of CTAB (0.02 M) and SG⁺ (1.6×10^{-5} M) and varying the concentration of sodium hydroxide in the reaction system. The values of pseudo first order rate constant as a function of hydroxyl ion concentration in the range of 0.0005 M to 0.0125 M are summarised in Table III.8.

b. Reaction between BG⁺ and hydroxyl ion: The effect of hydroxyl ion concentration on the reaction rate for the alkaline fading of BG⁺ carbonium ion was studied by keeping the concentrations of CTAB (0.02 M) and the substrate (1.6×10^{-5} M) fixed and varying the BG⁺ concentration in the reaction system. The kinetic data exhibits the hydroxyl ion dependence of the rate constant in presence of CTAB are summarised in Table III.8.

c. Reaction between MG⁺ and hydroxyl ion: The effect of reactant concentration on the pseudo first order rate constant for the reaction of MG⁺ carbonium ion with hydroxyl ion was studied at fixed concentrations of CTAB (0.02 M) and the substrate (1.6×10^{-5} M) and varying MG⁺ concentration in the reaction system. The kinetic data for the effect of hydroxyl ion concentration on reaction rate are summarised in Table III.8.

Table III.8. Pseudo first order rate constant, k_{ψ} , as a function of hydroxyl ion concentration in presence of 0.02 M CTAB for the alkaline fading reaction of triphenylmethyl carbonium ions at 25°C.

Sl. No.	$[\text{OH}^-] \times 10^4$	First Order Rate Constant $k_{\psi} \times 10^2 \text{ min}^{-1}$		
		$[\text{SG}^+] = 1.6 \times 10^{-5} \text{ M}$	$[\text{BG}^{++}] = 1.6 \times 10^{-6} \text{ M}$	$[\text{MG}^+] = 1.6 \times 10^{-5} \text{ M}$
1.	0.5		4.86	3.23
2.	1.0			3.33
3.	1.5		10.02	4.55
4.	2.0			7.89
5.	3.0		17.71	11.09
6.	4.0		25.59	16.92
7.	5.0	7.54		
8.	6.0		50.70	33.68
9.	7.5	4.55		
10.	8.0		91.33	60.66
11.	10.0	6.04	134.40	89.56
12.	15.0	9.59	192.32	177.40
13.	20.0	19.35		227.70
14.	30.0	29.25		
15.	40.0	40.08		
16.	50.0	51.20		
17.	75.0	77.76		
18.	100.0	104.80		
19.	125.0	139.30		

d. General features of rate vs reactant concentration profile:

It may be observed from Table III.8 and also Fig. III.7 that the increasing concentration of hydroxyl ion in the reaction system on the reactions of SG^+ , BG^+ and MG^+ carbonium ions in presence of CTAB has the effect of increasing the value of pseudo first order rate constant. In case of reaction of MG^+ and BG^+ at lower hydroxyl concentration the increase was not much however at comparatively higher hydroxylion concentration the rate constant varies linearly only in a narrow concentration range of hydroxyl ion. Similar results were obtained for the reaction of SG^+ carbonium ion with hydroxyl ion. A better insight into rate vs reactant concentration profile may be obtained by introducing the concept of catalysis factor, defined as,

$$\text{Catalysis Factor, C.F.} = \left(\frac{k_{\psi}}{k_w} \right) [\text{OH}^-] = \text{constant} \quad \dots (3.6)$$

where k_w is pseudo first order rate constant in absence of detergent and k_{ψ} , the value of first order rate constant in presence of detergent corresponding to saturation value in rate vs surfactant concentration profile. The values of rate constant k_w and k_{ψ} correspond to same total reactant concentration in the reaction system.

The values of catalysis factor as a function of hydroxyl ion concentration for various reactions viz., reaction of SG^+ , BG^+ and MG^+ carbonium ion hydroxyl ion in presence of 0.02 M CTAB are summarised in Table III.9. It may be noted from this table

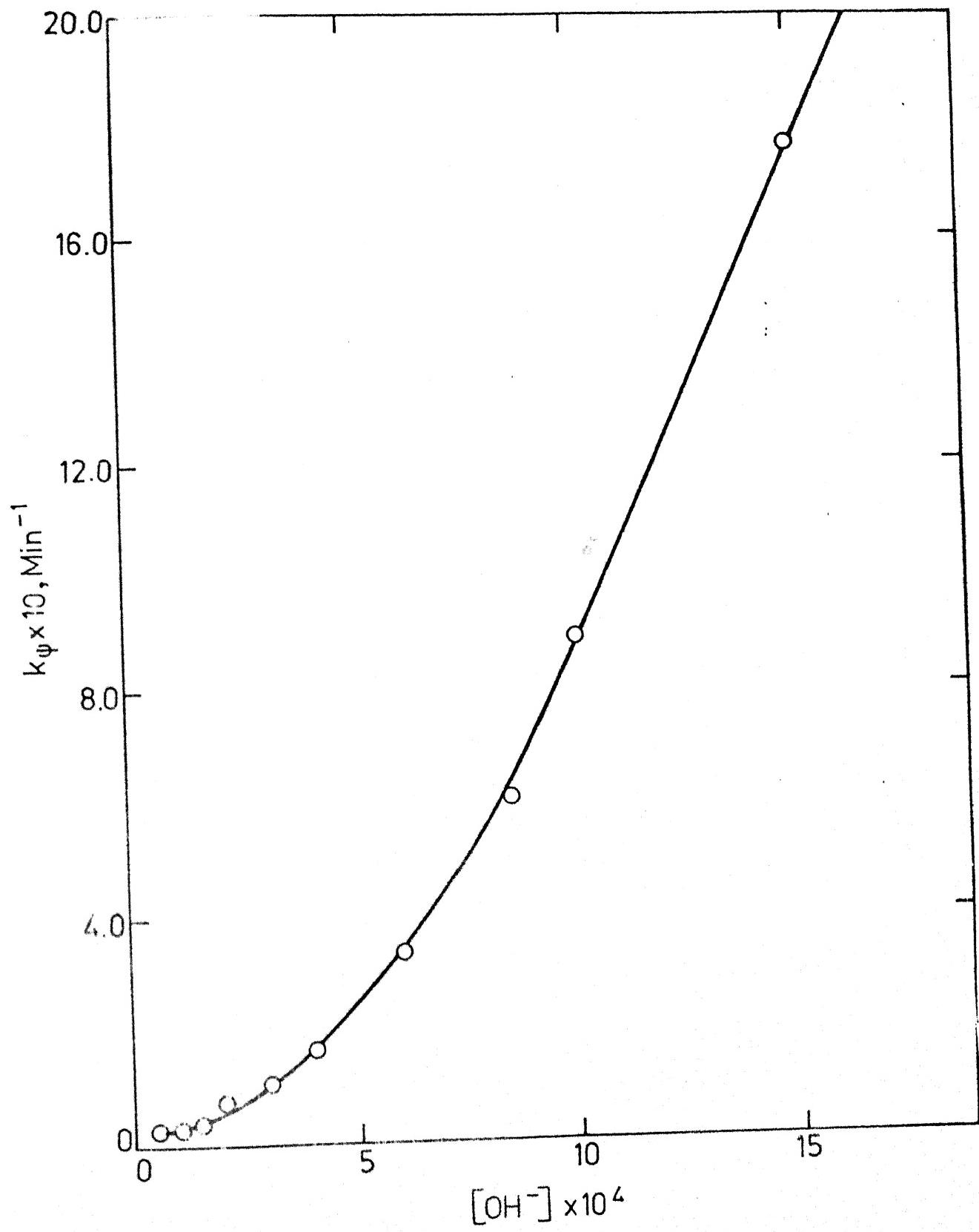


Fig. III.7 Rate vs hydroxyl ion concentration profile for the alkaline fading reaction of MG^+ carbonium ion in presence of 0.02M CTAB at 25°C .

Table III.9. The values of overall catalysis factor as a function of hydroxyl ion concentration for alkaline fading reaction of carbocations in presence of 0.02 M CTAB at 25°C

Sl.No.	$[\text{OH}^-] \times 10^4$	Overall catalysis factor for alkaline fading reaction of		
		$[\text{SG}^+] \text{ ion}$	$[\text{BG}^+] \text{ ion}$	$[\text{MG}^+] \text{ ion}$
1.	0.5		3.45	5.84
2.	1.0		3.04	3.01
3.	1.5			2.74
4.	2.0		5.64	3.57
5.	3.0		7.46	3.34
6.	4.0		9.25	3.83
7.	7.0	7.54		
8.	6.0		14.29	5.078
9.	7.5	18.60		
10.	8.0		21.03	6.86
11.	10.0	18.52	26.22	8.10
12.	15.0	19.40	28.19	10.40
13.	20.0	29.60		10.30
14.	30.0	29.89		
15.	40.0	30.72		
16.	50.0	31.40		
17.	75.0	31.76		
18.	100.0	32.13		
19.	125.0	34.17		

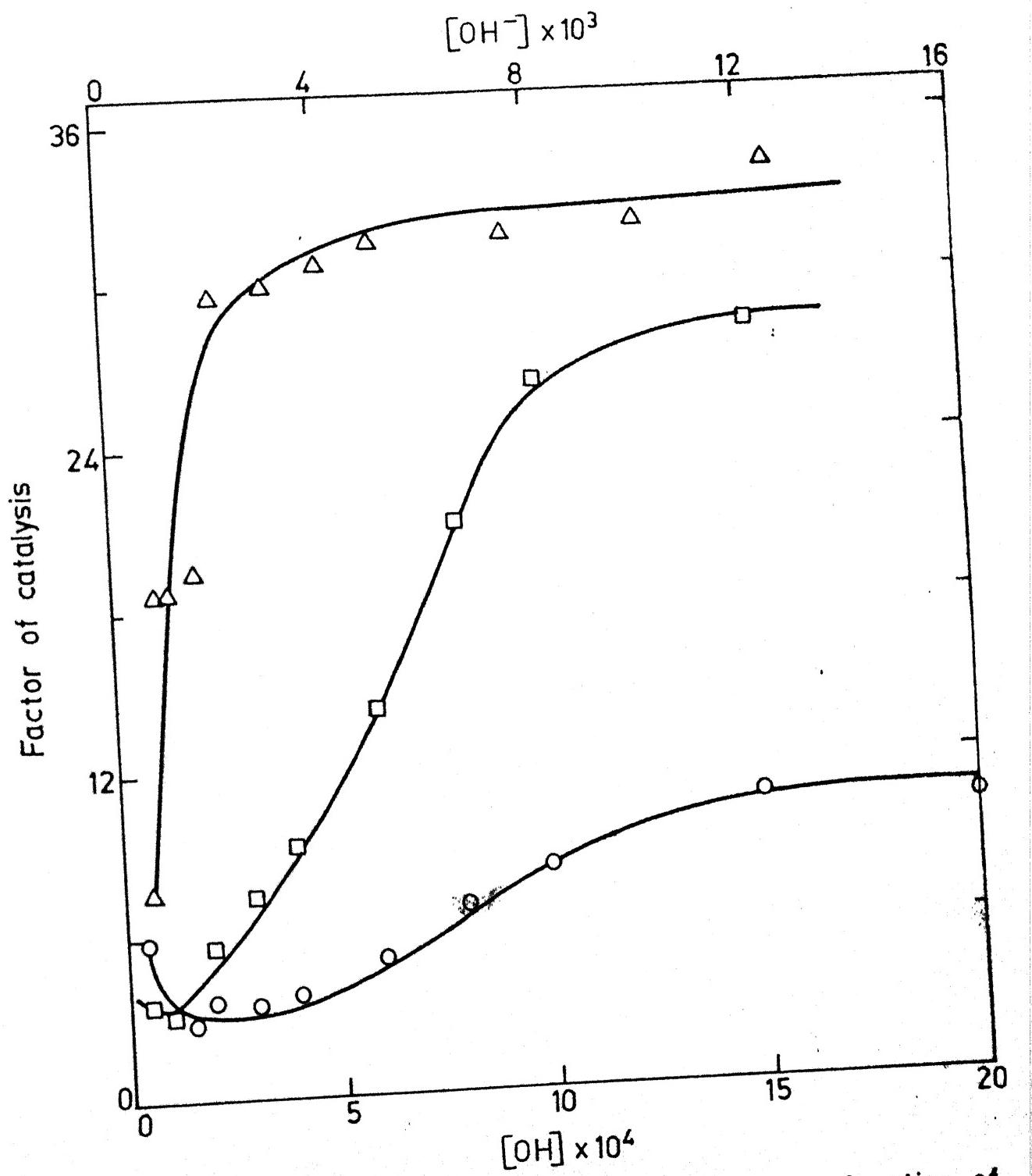


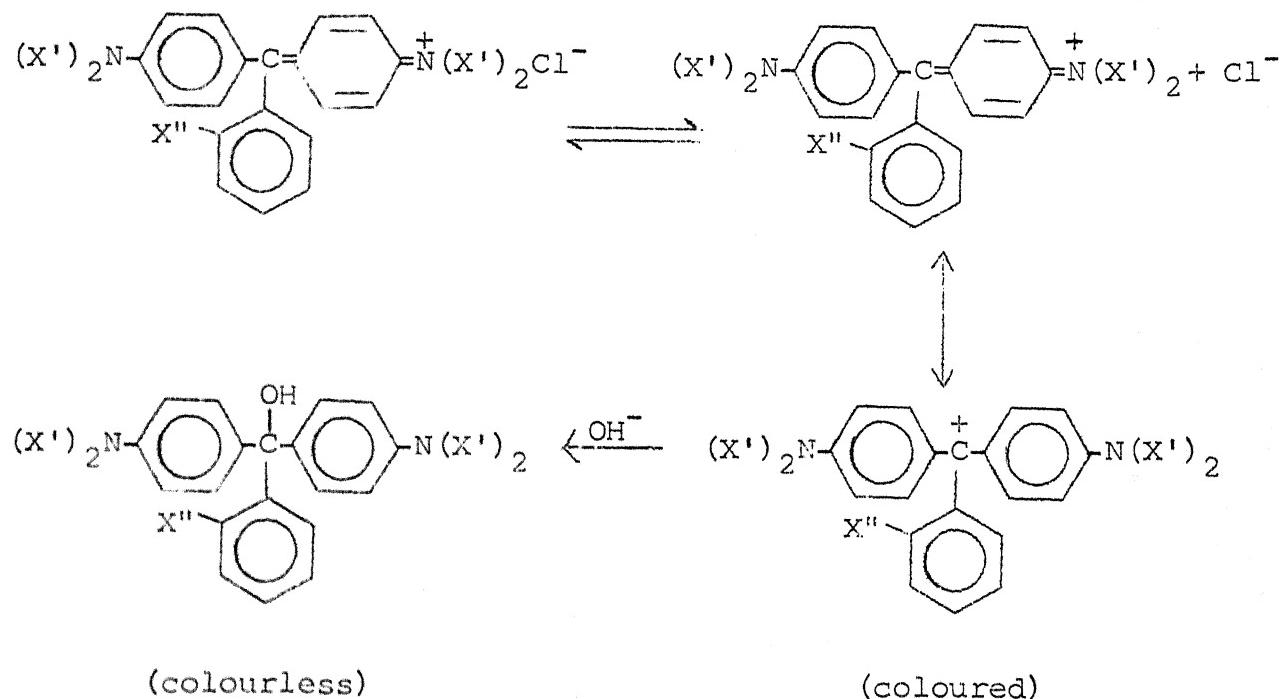
Fig. III.8 Variation of overall catalysis factor as a function of hydroxyl ion concentration for alkaline fading reaction of SG^+ (Δ), BG^+ (\square) and MG^+ (\circ) carbonium ions in presence of 0.02M CTAB at 25°C.

as well as from Fig. III.8 that at low hydroxyl ion concentration the values of catalysis factor for these reactions are low. For the alkaline fading reactions of BG^+ and MG^+ carbonium ions, which occur at lower hydroxyl ion concentration as compared to that of alkaline fading reaction of SG^+ carbonium ion, the value of catalysis factor in the beginning decreases slightly with increasing hydroxyl ion concentration at very low (≈ 0.001 M) reactant concentration. As hydroxyl ion concentration in the reaction system is further increased the value of catalysis factor for all the three reactions increase steeply tending to result in final saturation value. Thus for triphenylmethyl carbonium ions reaction with hydroxyl ion the optimal reactant concentration may be chosen at which maximum rate enhancement would be observed in presence of cationic micelle surfactant. A further increase in the reactant concentration would have insignificant effect upon the overall enhancement of the reaction rate in presence of cationic surfactant.

III.6 DISCUSSION

III.6.1 Reaction Mechanism

The alkaline fading reaction of triphenylmethane dyes is two step process represented as follows:



where $\text{X}' = \text{CH}_3$ and $\text{X}'' = \text{Cl}$ for SG;
 $\text{X}' = \text{C}_2\text{H}_5$ and $\text{X}'' = \text{H}$ for BG;
 $\text{X}' = \text{CH}_3$ and $\text{X}'' = \text{H}$ for MG.

In the first step the dye cation with unit positive charge is produced and it does not contribute to the rate process. The carbocation then reacts with hydroxyl ion present in the reaction system to form colourless carbinol.

III.6.2 Micellar Effects on the Reaction Rate

The reaction of carbonium ions viz., SG^+ , BG^+ and MG^+ with hydroxyl ion is inhibited upon the addition of SDS in the reaction system. In contrast the addition of CTAB in the reaction system catalyses these reactions and thus the reaction rate in presence of this detergent increases. The first order nature of these

reactions in presence of micelle-forming surfactants is demonstrated by the substrate concentration vs rate profile. The plot of overall inhibition factor for these reactions vs hydroxyl ion concentration in presence of SDS goes through a maximum which afterwards tends to attain saturation value (Fig. III.4). In presence of CTAB the overall catalysis factor for these reactions increases with increasing hydroxyl concentration, except at very low hydroxyl ion concentration, which afterwards tends to attain a final saturation value (Fig. III.8). In the range of very low hydroxyl ion concentration the value of overall catalysis factor in presence of CTAB decreases with increasing hydroxyl ion concentration giving rise to a minimum in the plot of overall catalysis factor vs reactant concentration. Such a minimum for the reaction of SG^+ with hydroxyl ion could not be obtained since the reaction of SG^+ with hydroxyl ion could be followed at relatively higher reactant concentration.

These observations may be rationalized by postulating (i) that the substrate, detergent, counter ion and/or reactant in the reaction system associate to form catalytically functional loose aggregates; (ii) that the substrate with higher hydrophobicity will involve more detergent molecules in the process of aggregation; (iii) that the ground state of the reaction may be more/less stabilized with respect to transition state as a result of the formation of catalytic aggregates; (iv) that increasing concentration of counter ion or reactant (in case reactant also serves as counter ion of the surfactant under consideration) in the reaction

system will neutralize the head group charge of the catalytic micelles and a further increase in counter ion or reactant concentration would result in the state of saturation with respect to charge neutralization and (v) that the alkaline fading reaction of triphenylmethyl carbonium ions obey Equation (3.4).

In presence of SDS in the reaction system the surfactant, the substrate i.e., SG^+ , BG^+ or MG^+ and the counter ion i.e., Na^+ may associate to form catalytically functional micelle with net negative charge. In this process of aggregation the reactant is excluded from the catalytic aggregates as hydroxyl ion lacks hydrophobicity and bears charge similar to that of surfactant head groups. As a result of formation of these catalytic aggregates the ground state of the reaction will be more stabilized with respect to transition state of the reaction and the hydroxyl ion will not be able to approach the carbonium ion due to unfavourable electrostatic interaction between reactant and the catalytic micelles. However, the aggregates and other species viz., substrate, detergent and the counter ion in the reaction system will be in the state of dynamic equilibrium and thus there exists finite, however small, probability of carbonium ions reacting with hydroxyl ion. The stabilization of ground state with respect to the transition state and non-approachability of hydroxyl ion are the factors responsible for inhibition observed in presence of SDS in the reaction system. The reactant vs rate profile can be explained by considering Equation (3.4). At low hydroxyl ion concentration the values of both the factors i.e.,

k_1 and $k_2 \cdot C_{OH}$ are suppressed in presence of SDS. The suppression in the value of k_1 is consistent with the observations of Duynstee and Grunwald.¹⁴ At higher sodium hydroxide concentrations the sodium ions will neutralize the head group charge of the catalytic micelles thereby facilitating the approach of hydroxyl ion to the carbonium ions in the catalytic aggregates. Further, the probability of attack of reactant hydroxyl ion upon the complexed carbonium ions increases with increase in overall hydroxyl ion concentration. As a result of this the value of overall inhibition factor decreases and thus gives rise to maximum in the plot of overall inhibition factor vs hydroxyl ion concentration. At higher sodium hydroxide concentration the saturation of the head groups of the catalytic micelles occurs with respect to charge neutralization. As a result of mutual hindrance in the reactant ions its concentration in the vicinity of catalytic micelles may not increase with further increase in total hydroxyl ion concentration in the reaction system. Thus the overall inhibition factor tends to attain a saturation value. The appearance of maximum in overall inhibition factor vs hydroxyl ion concentration profiles indicates that there is an optimum reactant concentration at which maximum inhibition would occur. In the region of optimal hydroxyl ion concentration the values of overall inhibition factor for these reactions varies in the order of substrate hydrophobicity viz., $SG^+ > BG^+ > MG^+$.

The catalysis in presence of CTAB may be explained by considering the formation of catalytic micelles with net positive

charge by the association of substrate, detergent, counter ion and reactant (hydroxyl ions) in the reaction system. Since the binding of hydroxyl ions with surfactant head groups is known to be weak, only a small fraction of the total hydroxyl ion concentration will be involved in the process of aggregation to form catalytic micelles.^{32,33} Inspite of this the reactant concentration around catalytic micelles would be increased as a result of favourable electrostatic interaction between catalytic aggregates and the hydroxyl ions. Further, the process of aggregation would have the consequence of destabilizing ground state with respect to transition state. Thus the increased reactant hydroxyl ion concentration around catalytic micelles and the destabilization of ground state of the reaction with respect to transition state may be assigned as the factor responsible for the observed catalysis in presence of CTAB for alkaline fading reaction of these carbocations.

The shape of curves resulting from the plot of overall catalysis factor vs hydroxyl ion concentration (Fig. III.8) may be explained on the basis of Equation (3.4). For the reaction of triphenylmethyl carbonium ions with hydroxyl ion in presence of CTAB the value of k_1 in Equation (3.4) is suppressed whereas the value of $k_2 \cdot C_{OH^-}$ is elevated.¹⁴ At very low hydroxyl concentration the contribution of k_1 is more than that of kC_{OH^-} towards the determination of overall rate constant in presence of detergent. This results in the decreasing value of overall catalysis factor. As the reactant concentration is further increased the

catalytic contribution due to term $k_2 \cdot C_{OH}^-$ overrides the suppression in the value of k_1 and thus the overall catalytic factor increases with increasing reactant concentration. At high reactant concentration the catalytic micelles tend to become saturated with hydroxyl ion and further increase in its concentration makes a small contribution towards the increase in overall catalysis factor. Thus, the curve at higher hydroxyl ion concentration tends to attain saturation value. It may be concluded that in this region of hydroxyl ion concentration the ratio of reactant concentration in complexed phase and the free bulk phase remains constant for these reactions in presence of CTAB. In the region of saturation (Fig. III.8), in the plots of overall catalysis factor vs hydroxyl ion concentration the values of catalysis factor could be arranged in the following decreasing order for the substrates viz., $SG^+ > BG^+ > MG^+$.

It is of interest to note that both overall inhibition factor and overall catalysis factor show identical decreasing trend in respect of substrates that is their values decrease for the substrates in the order $SG^+ > BG^+ > MG^+$. This suggests that the hydrophobicity of these substrates could be arranged in a similar order $SG > BG > MG$. A comparison of the structure of these dyes thus indicates that the introduction of Cl group in the phenyl ring to form SG imparts more hydrophobicity to the substrate than does the replacement of CH_3 groups by C_2H_5 groups to form BG.

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CHAPTER IV

MICELLAR EFFECTS ON THE REACTION OF TRIPHENYLMETHYL
CARBONIUM IONS WITH HYDROXYL ION: INVESTIGATION
AND ANALYSIS OF COUNTER ION EFFECTS

IV.1 ABSTRACT

The overall efficiency of micellar effects on the reaction rates of triphenylmethyl carbonium ions viz., SG^+ , BG^+ and MG^+ with hydroxyl ion is diminished upon the addition of counter ions to the reaction systems. The influence of counter ions viz., Li^+ , Na^+ and Rb^+ which was studied at relatively higher sodium hydroxide concentration, on the alkaline fading reaction of SG^+ carbonium ion in presence of SDS was found insignificant. The value of pseudo first order rate constant for SDS inhibited reaction of BG^+ and MG^+ carbonium ions with hydroxyl ion increases with increasing concentration of cations viz., Li^+ , Na^+ , Rb^+ and Cs^+ . The counter ions viz., CH_3COO^- , Cl^- , Br^- , NO_3^- and N_3^- reduce the extent of overall catalysis of the reaction of considered triphenylmethyl carbonium ions with hydroxyl ion in presence of CTAB.

The kinetic data for the influence of counter ions on micellar effects of these reactions have been analysed following the model schemes developed in Chapter II. Analysis of the data on the basis of Scheme II.1 indicate that the neutralization of charges on the catalytic micelles and the alteration in the thermodynamic parameters of the reactions are factors responsible for the observed counter ions effect on the inhibition of the alkaline fading reaction of triphenylmethyl carbonium ions in presence of SDS. Quantitative analysis of the effect of anions on the micellar catalysis of these reactions in presence of CTAB was done by using equations developed by formulating Scheme II.2. The values of various parameters used in this model scheme for these reaction

systems clearly indicate that the effect of counter ions in reducing the overall catalytic efficiency of CTAB may be attributed to the perturbation of thermodynamic parameters of the reactions and the replacement of reactant hydroxyl ions by inert counter ions from the vicinity of catalytic micelles. The replacement of the substrate from the complexed phase to aqueous bulk phase is unambiguously ruled out as the neutralization of charges on catalytic micelles by counter ion would reduce the repulsive electrostatic interaction between substrates viz., SG^+ , BG^+ and MG^+ and the cationic micelle-forming detergent CTAB, resulting in the enhancement of the binding. Further, it has been inferred that the composition of catalytic micelles corresponding to various substrates in presence of ~~the~~ same surfactant, counter ion and reactant species may not be the similar and that the degree of ionic dissociation of catalytic micelles in a given reaction system is dependent on the specific interactions of the counter ions present therein with catalytic aggregates.

IV.2 INTRODUCTION

One of the vital and notable aspects of micellar catalysis of chemical reactions is their sensitivity to salt effects.¹⁻¹² Added electrolytes to the reaction system containing micelle-forming surfactant have been found to alter the efficiency of micellar effects through the participation of counter ions. The influence of electrolytes on a number of reactions has been examined and certain common features have been noticed viz., (i) that

the salt effects are specific and depend upon the nature of the ion which has the charge opposite to that of the catalytic micelle; (ii) that the effects are relatively independent of the nature and structure of co-ion i.e., the ion bearing the charge similar to that of catalytically functional micelles; (iii) that the effectiveness of counter ion in changing the overall efficiency of catalytic micelles depends upon the position of counter ion in lyotropic series i.e., the effects are greatest for large, low charge density ions which interact most strongly with the catalytically functional micelles; (iv) that the relative effectiveness of counter ions in modifying the micellar effects is largely independent of the chemical reaction under scrutiny and (v) that the counter ion, generally, reduce the overall extent of micellar catalysis, however, a few exceptions to this general behaviour have been reported recently.¹³

The effect of sufficiently hydrophobic and negatively charged counter ions on the reaction of negatively charged substrate with a nucleophile in presence of a cationic micelle-forming surfactant was treated by Bunton *et al.*⁴ by extending the Menger and Portnoy model of micellar catalysis by assuming competitive binding between the substrate and the counter ions with the micelles. However, this treatment cannot be applied to other reaction systems for the quantitative analysis of the effect of counter ions on micellar catalysis because the physical realities which exist in the reaction systems, in general, do not conform to the assumptions made in this formulation. For example, the

possibility of the replacement of hydrophobic substrate by hydrophilic counter ions from complexed phase to bulk of the solution seems unreal, and the deactivation of a micelle completely as a result of its association with a single counter ion may be an oversimplified assumption. Moreover, some other factor which do contribute to overall effects viz., (i) neutralization of charges on the catalytic micelles by counter ions; (ii) replacement of reactant ion species around the catalytic micelles by inert counter ions and vice-versa as a result of the variation of concentration of these species in the reaction system; (iii) changes in the thermodynamic parameters of the reaction in micellar environment and (iv) the possible changes in the aggregation properties of the detergent to form catalytic micelles in presence of electrolytes and substrate etc, were not considered in this treatment.

The method developed by Srirahamā¹⁴ for the analysis of the effect of added electrolytes on micellar catalysis does not attempt to explain the specific effects i.e., the difference in the relative overall effectiveness of various counter ions in altering micellar effects. Berezin et al.¹⁵ also do not treat reaction systems where specific ionic effects are important. The treatment of Romsted¹⁶ makes an assumption that the degree of counter ion binding to the micelles is constant however, the recent experimental results of Almgren and Rydholm¹⁷ show that this may not be true. Further, it may be pointed out that if the degree of counter ion binding is assumed constant then this

implies that the various counter ions are identical in relation to their interactions. Therefore, they should neutralize micellar surface charges to the same extent. However, the results of counter ion effects on micellar catalysis clearly show that the specific ionic interactions are important.

In this chapter the experimental studies in the effect of counter ions on sodium dodecyl sulfate (SDS) inhibited and cetyltrimethylammonium bromide (CTAB) catalysed reaction of triphenylmethyl carbonium ions viz., SG^+ , BG^+ and MG^+ with hydroxyl ion are reported. The experimentally obtained kinetic data for micellar effects have been analyzed on the basis of our recently proposed schemes (described in Chapter II). The values of equilibrium binding constant of the substrates with the detergents, i.e., SDS and CTAB, in presence of various counter ions have been calculated. Further, the values of equilibrium exchange factor $f.K_e$, for the exchange between different anions and reactant hydroxyl ion, in presence of CTAB are reported. The number n and p, analogous to cooperativity index in enzymatic reaction, corresponding to detergents and various counter ions have been evaluated.

IV.3 EXPERIMENTAL SECTION

IV.3.1 Method and Reagents

The method used for the evaluation of rate constant and the purity of chemicals used in this study are described in Chapter III.

IV.3.2 Analysis of Kinetic Data

The analysis of experimental data was done using Computer, DEC system 1090 (model KL-10) on the basis of mathematical formulation developed in Chapter II.

IV.4 RESULTS

IV.4.1 EFFECT OF COUNTER IONS ON SDS INHIBITED REACTION OF TRIPHENYLMETHYL CARBONIUM IONS WITH HYDROXYL ION

It has been reported in Chapter III that the alkaline fading reactions of triphenylmethyl carbonium ions viz., SG^+ , BG^+ and MG^+ are inhibited upon the introduction of SDS in the reaction system. The effect of counter ions viz., Li^+ , Na^+ , Rb^+ and Cs^+ on these reactions in presence of SDS was examined at fixed concentrations of detergent, reactant and the substrate by varying the concentration of counter ions in the reaction systems. The fixed concentration of detergent corresponds to saturation concentration of SDS in rate vs detergent concentration profile for these reactions. The effect of K^+ on these reactions in micellar environment could not be studied as this ion precipitates the detergent from the solution.

a. Alkaline fading reaction of SG^+ carbonium ion: The effect of counter ions viz., Li^+ , Na^+ and Rb^+ on the SDS inhibited reaction of SG^+ carbonium ion with hydroxyl ion was studied at constant concentrations of SDS (0.005 M), hydroxyl ion (0.5 M) and substrate (6.0×10^{-6} M) by varying the concentration of counter ions in the reaction system. The results are summarized in Table IV.1.

Table IV.1. Effect of cations on alkaline fading reaction of triphenylmethyl carbonium ions in presence of 0.005 M SDS at 25°C

Sl. No.	Counter Ion Concentration, M	First order rate constant, $k_{\text{H}} \times 10^3 \text{ min}^{-1}$			
		Li^+	Na^+	Rb^+	Cs^+
1	2	3	4	5	6

Reaction of SG⁺ Carbonium Ion

$$[\text{OH}^-] = 0.5 \text{ M} \quad [\text{SG}^+] = 6 \times 10^{-5} \text{ M}$$

1.	0.00	3.97	3.97	3.97
2.	0.02	3.97	3.97	3.97
3.	0.05	4.02	4.03	
4.	0.10	4.02	4.02	
5.	0.15	3.97	3.97	

Reaction of BG⁺ Carbonium Ion

$$[\text{OH}^-] = 0.01 \text{ M} \quad [\text{BG}^+] = 8 \times 10^{-6} \text{ M}$$

1.	0.000	5.30	5.30	5.30	5.30
2.	0.005			6.29	
3.	0.010			7.21	
4.	0.015			7.16	
5.	0.020			7.89	
6.	0.030				8.98
7.	0.040	8.36	8.98		
8.	0.08	11.05	12.43		13.31

...contd.

Table IV.1 (contd.)

1	2	3	4	5	6
9.	0.10	11.51	12.52		
10.	0.11				15.07
11.	0.15				17.13
12.	0.16	13.82	15.36		
13.	0.20	15.93	17.73		
14.	0.25	15.91	17.73		23.31

Reaction of Mg^+ Carbonium Ion

$$[\text{OH}^-] = 0.01 \text{ M} \quad [\text{Mg}^+] = 8 \times 10^{-6} \text{ M}$$

1.	0.00	10.07	10.07	10.07	10.07
2.	0.005				12.00
3.	0.01				14.00
4.	0.015				17.65
5.	0.02				18.42
6.	0.03		17.9		22.56
7.	0.04	16.4			
8.	0.05				26.61
9.	0.06	19.8	22.66		
10.	0.08				30.19
11.	0.09	22.45	26.01		
12.	0.11				
13.	0.12	24.18	28.25		
14.	0.15	28.09	29.94		33.30

b. Alkaline fading reaction of BG⁺ carbonium ion: The effect of cations viz., Li⁺, Na⁺, Rb⁺ and Cs⁺ on the micellar inhibition of the alkaline fading reaction of BG⁺ carbonium ion was investigated by keeping the concentrations of SDS (0.005 M), hydroxyl ion (0.01 M) and substrate (6×10^{-6} M) fixed and varying the counter ion concentration. The effect of these counter ion is exhibited in Fig. IV.1. The kinetic data are also summarized in Table IV.1.

c. Alkaline fading reaction of MG⁺ carbonium ion: The effect of counter ions viz., Li⁺, Na⁺, Rb⁺ and Cs⁺ on the micellar inhibition of the reaction of MG⁺ carbonium ion with hydroxyl ion in presence of SDS was examined by keeping the concentrations of detergent (0.005 M), reactant (0.01 M) and the substrate (8×10^{-6} M) constant and varying the concentration of counter ion in the reaction system. The values of rate constant as a function of counter ion concentration are summarized in Table IV.1 and also shown in Fig. IV.2.

d. General features of the effect of cations on SDS inhibited alkaline fading reaction of triphenylmethyl carbonium ion: It may be noted from the data of Table IV.1 and Figs. IV.1 and IV.2 that the counter ions do not exhibit significant influence on the reaction of SG⁺ carbonium ion with hydroxyl ion in presence of SDS. For the reaction of BG⁺ and MG⁺ carbonium ions with hydroxyl ion in presence of SDS the value of pseudo first order rate constant increases with increasing cation concentration and finally reaches a saturation value. This shows that the extent of

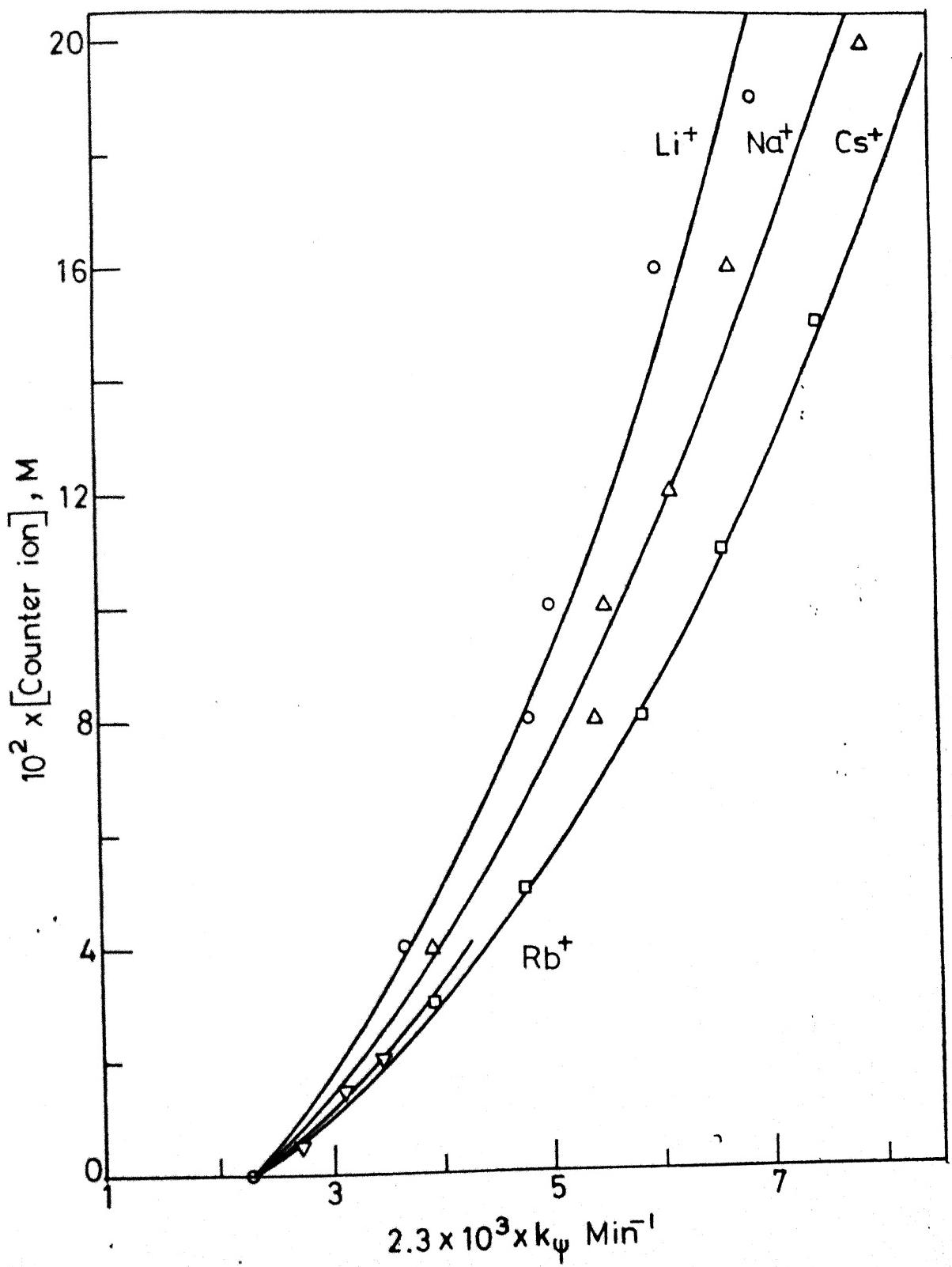


Fig. IV.1 The effect of cations on sodium dodecyl sulphate inhibited reaction of Brilliant green carbonium ion with hydroxyl ion at 25°C .

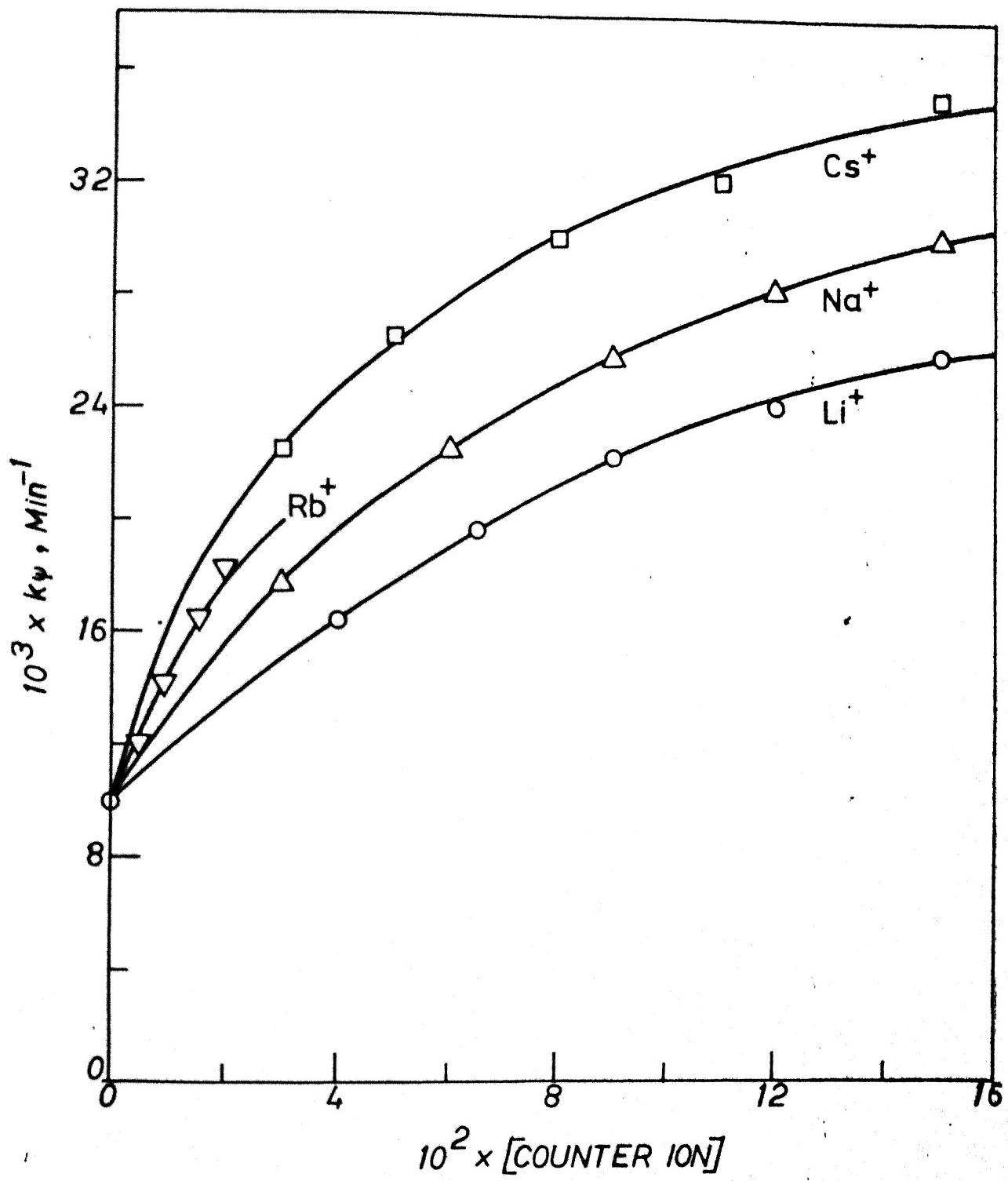


Fig. IV.2 The effect of counter ion on sodium dodecyl sulphate inhibited alkaline fading reaction of Malachite Green carbonium ion at 25°C .

inhibition, caused due to the presence of detergent, is reduced as the concentration of counter ions viz., Li^+ , Na^+ , Rb^+ and Cs^+ is increased in the reaction system. At a given cation concentration overall effectiveness of the counter ions in modifying the extent of micellar catalysis was found in the increasing order of $\text{Li}^+ < \text{Na}^+ < \text{Rb}^+ < \text{Cs}^+$.

IV.4.2 EFFECT OF COUNTER IONS ON CTAB CATALYSED REACTION OF TRIPHENYLMETHYL CARBONIUM IONS WITH HYDROXYL ION

The effect of various anions on the catalysis caused by the presence of CTAB on the alkaline fading reactions of SG^+ , Bg^+ and MG^+ carbonium ions was studied by keeping the concentrations of detergent, reactant and the substrate constant and varying the counter ion concentration in the reaction system. The concentration of the detergent was chosen such that it corresponds to saturation concentration of CTAB in the rate vs surfactant concentration profile.

a. Reaction of SG^+ carbonium ion with hydroxyl ion: The effect of counter ions viz., Cl^- , Br^- , NO_3^- and N_3^- on the micellar catalysis of the alkaline fading reaction of SG^+ carbonium ion in presence of CTAB was studied at fixed concentrations of detergent (0.02 M), hydroxyl ion (0.01 M) and substrate (1.6×10^{-5} M) by varying the counter ion concentration in the reaction system. The values of pseudo first order rate constant as a function of counter ion concentration in presence of CTAB for this reaction are summarized in Table IV.2. The effect is also shown in Fig. IV.3.

Table IV.2. The values of pseudo first order rate constant for alkaline fading reaction of triphenylmethyl carbonium ions in presence of 0.02 M CTAB at 25°C.

Sl. No.	Counter Ion Concentration, M	First order rate constant, $k_{\psi} \times 10^{-1}$ min ⁻¹				
		Ac ⁻	Cl ⁻	Br ⁻	NO ₃ ⁻	N ₃ ⁻
1	2	3	4	5	6	7

Reaction of SG⁺ Carbonium Ion

$$[\text{SG}^+] = 1.6 \times 10^{-5} \text{ M}$$

$$[\text{OH}^-] = 0.01 \text{ M}$$

$$k_w = 4.48 \times 10^{-2} \text{ min}^{-1}$$

1.	0.00					
2.	0.01					4.15
3.	0.02		7.14	4.92		3.89
4.	0.04					1.98
5.	0.05		4.49	2.72	1.90	
6.	0.06					1.54
7.	0.08		3.76		1.41	
8.	0.10			1.41		1.09
9.	0.12		2.80		0.95	
10.	0.15					0.66
11.	0.16		2.02		0.83	
12.	0.20		1.82		0.74	0.47

Reaction of BG⁺ Carbonium Ion

$$[\text{BG}^+] = 1.8 \times 10^{-5} \text{ M}$$

$$[\text{OH}^-] = 0.001 \text{ M}$$

$$k_w = 5.14 \times 10^{-2} \text{ min}^{-1}$$

1.	0.00	8.35	8.35	8.35	8.35	
2.	0.025	7.20	6.25	4.04	3.40	... contd.

Table IV.2 (contd.)

1	2	3	4	5	6	7
3.	0.050	6.28	4.40	2.50	2.00	
4.	0.075	5.64	3.76	2.10	1.89	
5.	0.100	5.20	3.08	1.99	1.80	
6.	0.150	4.38	2.32	1.64	1.44	
7.	0.200	4.15	2.07	1.58		

Reaction of Mg^+ Carbonium Ion

$$[\text{Mg}^+] = 1.8 \times 10^{-5} \text{ M}$$

$$[\text{OH}^-] = 0.001 \text{ M}$$

$$k_w = 8.92 \times 10^{-2} \text{ min}^{-1}$$

1.	0.00	6.70	6.70	6.70	6.70	
2.	0.01		5.83			
3.	0.02				3.21	
4.	0.025			4.05		
5.	0.03		5.11			
6.	0.04		4.71		2.45	
7.	0.05		4.63	3.05		
8.	0.075		3.68	2.15		
9.	0.080				2.17	
10.	0.10		3.61	2.55	1.96	
11.	0.15		3.22	2.37	1.55	
12.	0.20		3.03		1.58	
13.	0.250			2.00		

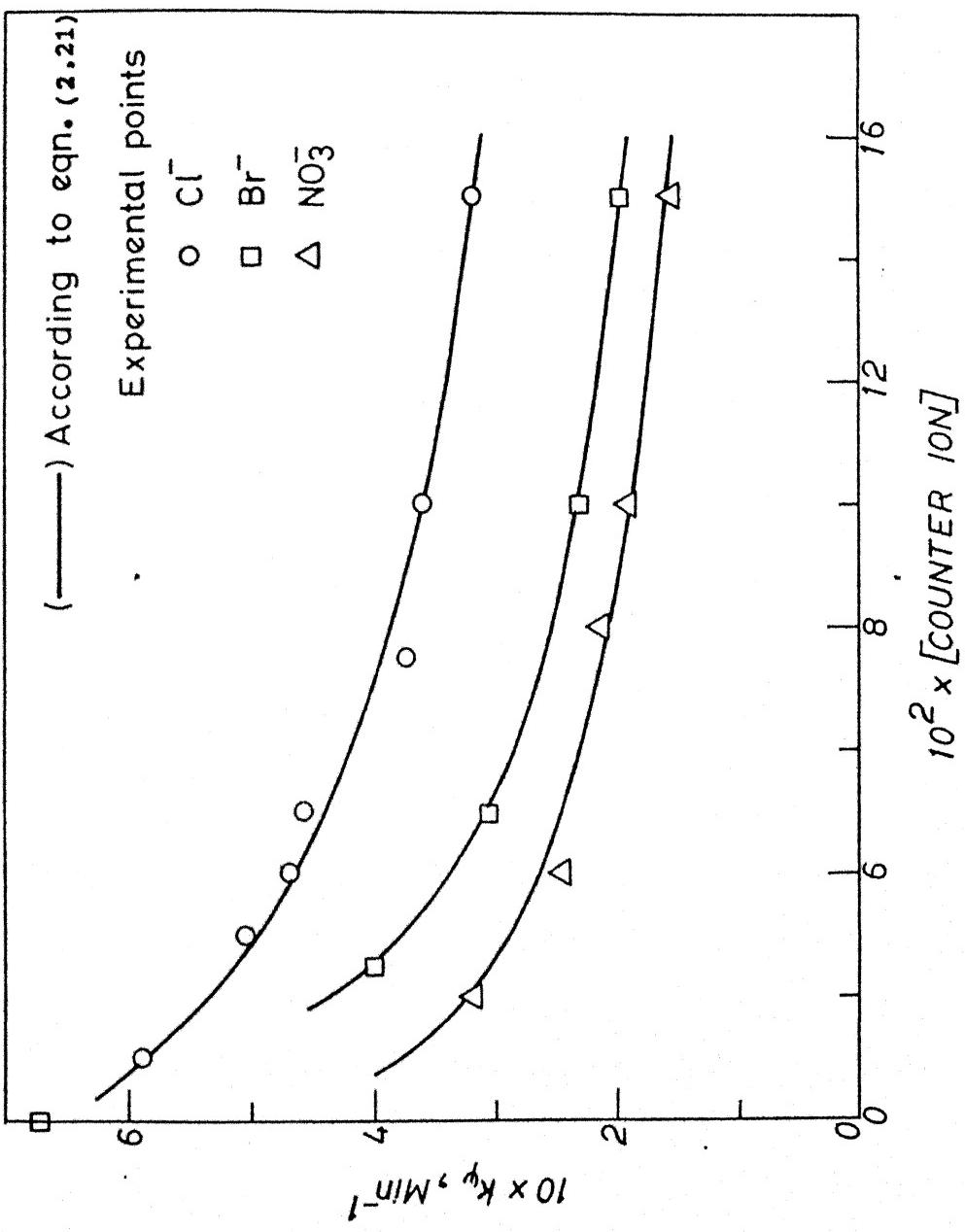


Fig. IV.3 The plots of pseudo first order observed rate constants for the effect of counter ions on CTAB (pre)micelle-catalyzed alkaline fading reaction of setoglaucine carbonium ion at 25°C.

b. Reaction of BG^+ carbonium ion with hydroxyl ion: The effect of anions viz., CH_3COO^- , Cl^- , Br^- and NO_3^- on the alkaline fading reaction of BG^+ carbonium ion in presence of CTAB was investigated by keeping the concentrations of detergent (0.02 M) hydroxyl ion (0.002 M) and substrate (1.8×10^{-5} M) constant and varying the concentration of counter ion in the reaction system. The effect is exhibited in Fig. IV.4 and the kinetic data concerning these studies are summarized in Table IV.2.

c. Reaction of MG^+ carbonium ion with hydroxyl ion: The effect of counter ions viz., CH_3COO^- , Cl^- , Br^- and NO_3^- on the micellar catalysis of the alkaline fading reaction of MG^+ carbonium ion in presence of CTAB was studied at fixed concentrations of detergent (0.02 M), reactant hydroxyl ion (0.001 M) and the substrate (1.8×10^{-5} M) by varying counter ion concentration. The kinetic data are summarized in Table IV.2 and are also exhibited in Fig. IV.5.

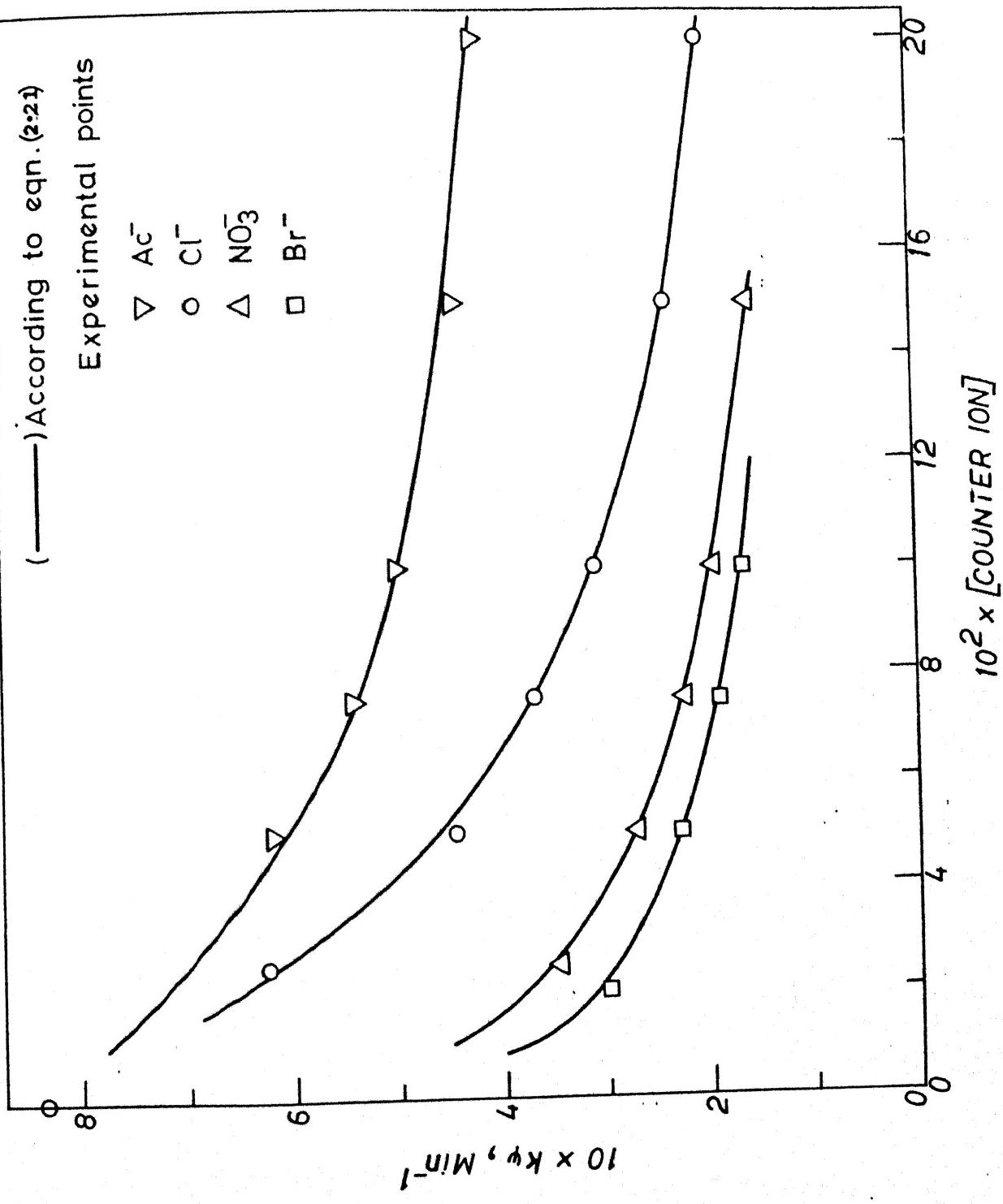
d. General features of the effect of anions on CTAB catalyzed alkaline fading reactions of triphenylmethyl carbonium ions:

Figures IV.4 and IV.5 and the Table IV.2 illustrate the effect of counter ions on the CTAB catalysed reaction of triphenylmethyl carbonium ions viz., SG^+ , BG^+ and MG^+ with hydroxyl ion. It may be inferred from the kinetic data that the addition of counter ions to the reaction system containing CTAB reduces the extent of overall catalysis caused by the presence of the detergent. In the initial stages the rate constant decreases steeply with increasing salt concentration but later on it tends to attain a saturation

(—) According to eqn. (2.2)

Experimental points

- ▽ Ac^-
- Cl^-
- △ NO_3^-
- Br^-



(—) According to eqn.(2.21)

Experimental points

- Cl^-
- Br^-
- △ NO_3^-
- ▽ N_3^-

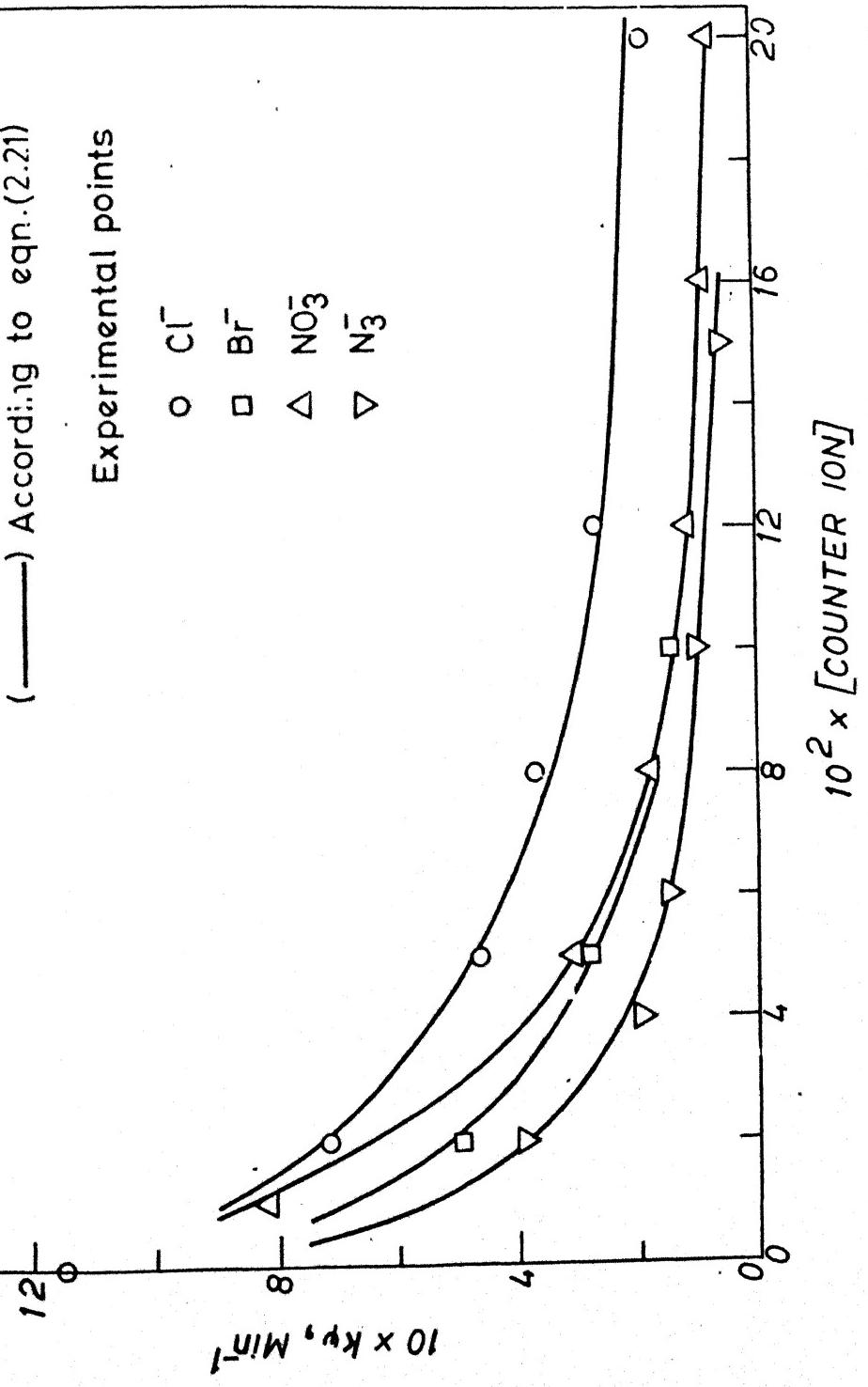


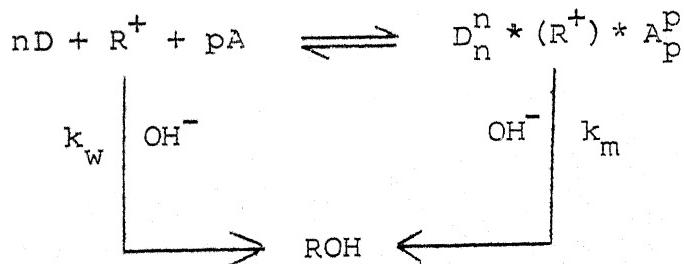
Fig. IV.5 The effect of anions on the reaction of Malachite Green carbocyanium ion with hydroxyl ion in presence of CTAB (pre)micelles at 25°C.

value. At a given counter ion concentration the ions having large size and low charge density are more effective in reducing the overall catalysis of the reactions investigated.

IV.4.3 ANALYSIS OF COUNTER ION EFFECTS ON SDS INHIBITED ALKALINE FADING REACTION OF TRIPHENYLMETHYL CARBONIUM IONS

The alkaline fading reactions of triphenylmethyl carbonium ions viz., SG^+ , BG^+ and MG^+ in a reaction system containing SDS and an electrolyte conform to Scheme II.1 described in Chapter II because of the existence of favourable electrostatic and hydrophobic interactions between substrate and the detergent and favourable electrostatic interaction between detergent and the counter ions i.e., cations. Thus, the surfactant, substrate and the counter ions associate to form catalytically functional aggregate. Reactant hydroxyl ions are excluded from the process of aggregation because of unfavourable electrostatic and absence of hydrophobic interactions between detergent and the reactant. Thus, the reaction of triphenyl carbonium ions with hydroxyl ion in presence of SDS may be represented as follows:^{18,19}

Scheme IV.1

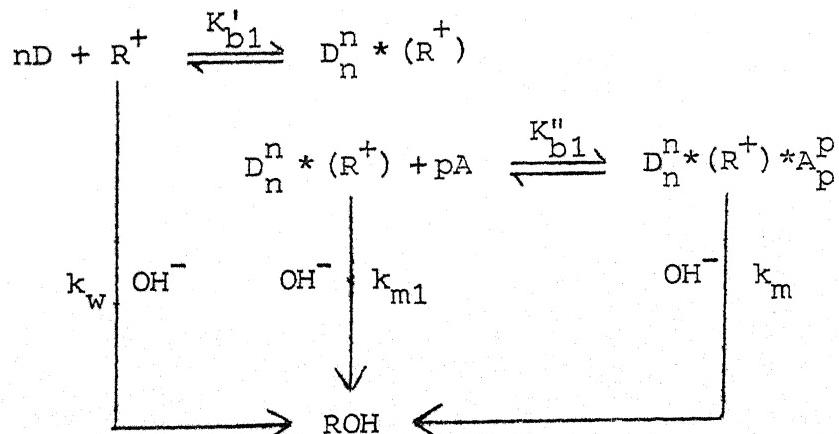


where R^+ is one of the carbonium ions SG^+ , BG^+ or MG^+ , D represents

hydrophobic anionic hydrocarbon chain of SDS, and A represents the counter ion i.e., cation given out by added electrolyte in the solution k_w and k_m are pseudo first order rate constants for free and complexed substrate respectively. K_{b1} being the equilibrium binding constant of the substrate with detergent in presence of counter ion A.

The aggregate $D_n^{n+} (R^+) * A_p^p$ is assumed to be a loose complex and the species present in it may constantly and continuously exchange with the species present in the bulk of the solution. Though the catalytically functional aggregates do not have the participation of hydroxyl ions in their formation but there exist a finite probability of the attack of hydroxyl ion on the complexed carbonium ion in solution. Consequently, the alkaline colour fading reaction of these carbonium ions proceeds in the forward direction in presence of SDS..

In actual reaction systems, multiple, sequential, equilibrium steps are involved in which substrate, detergent and the counter ions aggregate to form catalytically functional micelles. The Scheme IV.1 may be imagined to involve following steps:



In the first step the detergent and the substrate associate to form $D_n^n*(R^+)$ which interacts with the counter ions present in the reaction system to form aggregate $D_n^n*(R^+)*A_p^P$. k_{m1} represents rate constant for alkaline fading reaction of carbonium ion when it is complexed with the detergent. K'_{b1} and K''_{b1} are equilibrium binding constants for two sequential steps represented in Scheme IV.1.

Thus, by analogy from Scheme II.1, one may write;

$$\log \left\{ \frac{k_w - k_\psi}{k_\psi - k_{m1}} \right\} = \log K'_{b1} + n \log C_D \quad \dots (4.1)$$

$$\log \left\{ \frac{k_{m1} - k_\psi}{k_\psi - k_m} \right\} = \log K''_{b1} + p \log C_D \quad \dots (4.2)$$

and $K_{b1} = K'_{b1} \cdot K''_{b1} \quad \dots (4.3)$

where k_ψ represents observed pseudo first order rate constant and C_D and C_A are concentrations of detergent and counter ion respectively.

Now, the analysis of the effect of variation of SDS concentration on the rate according to Equation (4.1) i.e., the plot of $\log \left\{ \frac{k_w - k_\psi}{k_\psi - k_m} \right\}$ vs $\log C_D$, should give straight line with the value of slope and intercept equal to n and $\log K'_{b1}$ respectively. It may be pointed here that in the analysis of the effect of detergent on the rate of reaction the effect of counter ions furnished by the surfactant itself has been neglected. In view of the larger effect of the detergent in comparison to that of counter ion furnished by detergent this assumption seems to be correct. The

values of K'_{b1} and k_m' , in principle, can not be measured at zero counter ion concentration but the values so obtained by considering the effect of counter ions furnished by surfactant may serve well, at least semiquantitatively, to analyze the micellar effects in such cases.

The plot of $\log \frac{(k_m' - k_\psi)}{(k_\psi - k_m)}$ vs $\log C_A$ according to Equation 4.2, for the effect of cations in presence of SDS should give straight line with the value of slope and intercept equal to p and $\log K''_{b1}$. The values of $\log K'_{b1}$ and $\log K''_{b1}$ can be used to evaluate the overall binding constant K_{b1} in presence of any of the cations under investigation. The flow chart for analysis of micellar effect on the basis of this scheme is described in Fig. II.1 in Chapter II.

In the case of the reaction of SG^+ carbonium ion with hydroxyl ion, the inhibition by SDS was studied at high reactant concentration (0.5 M). The addition of counter ions was found to have no effect on the reaction rate in this reaction system. The analysis of micellar data for the effect of SDS concentration on the reaction of MG^+ and BG^+ carbonium ions with hydroxyl ion was done on the basis of Equation 3.1. Figure IV.6 shows the plot of $\log \frac{(k_w - k_{\psi_i})}{(k_\psi - k_m)}$ vs $\log C_D$. The values of n and $\log K'_{b1}$ for these reaction were evaluated from the slope and intercept respectively. The analysis of the effect of counter ion concentration in presence of SDS was done on the basis of Equation IV.2 to obtain the values of p and $\log K''_{b1}$ for these reactions. The plot of $\log \left\{ \frac{k_m' - k_\psi}{k_\psi - k_m} \right\}$ vs $\log C_A$ for the reaction of BG^+ carbonium ion

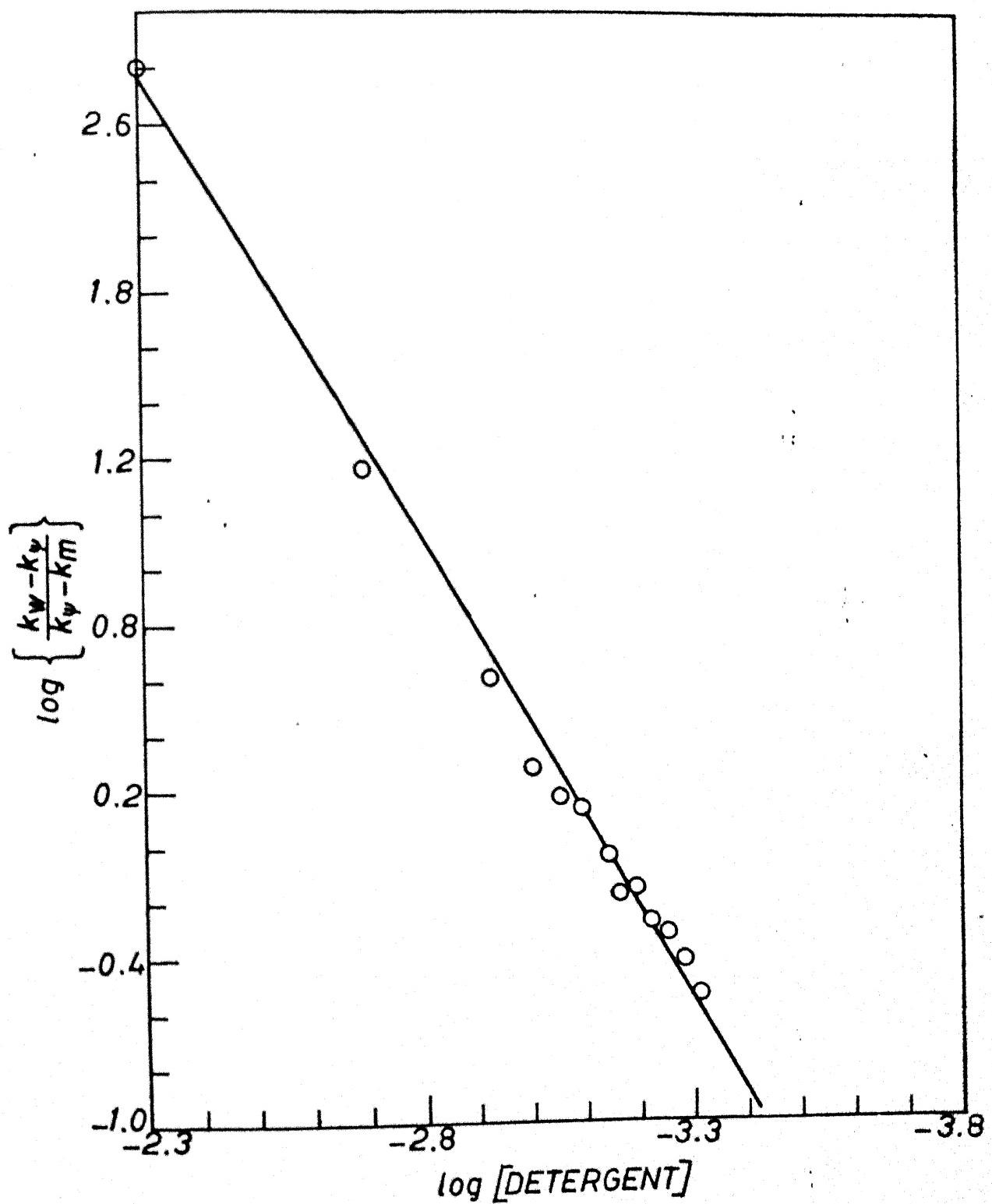


Fig. IV.6 Analysis of the effect of detergent concentration on the SDS (pre)micelle-inhibited alkaline fading reaction of MG^+ carbonium ion at 25°C .

with hydroxyl ion is shown in Fig. IV.7. The values of $\log K'_{b1}$ and $\log K''_{b1}$ were used to evaluate overall binding constant K_{b1} in presence of each of the counter ions. The values of n , p and K_{b1} for these reaction corresponding to various counter ions in presence of SDS are summarized in Table IV.3. It may be noted that the values of p and K_{b1} for these reactions increase in the order of increasing size and low charge density of the counter ions.

IV.4.4 ANALYSIS OF COUNTER ION EFFECTS ON CTAB CATALYSED ALKALINE FADING REACTION OF TRIPHENYLMETHYL CARBONIUM IONS

The observation of micellar catalysis in the reaction of positively charged triphenylmethyl ions viz., SG^+ , BG^+ and MG^+ with hydroxyl ion in presence of surfactant CTAB forming positively charged micelles, undoubtedly demonstrates the existence of predominantly hydrophobic interactions between the substrate and the detergent in comparison to the unfavourable electrostatic interactions. Further, there exists an attractive electrostatic interaction of detergent with the reactant as well as with the counter ion. Consequently, the substrate, detergent, counter ions and the reactant may associate to form catalytically functional micelles. The species present in these aggregates will be in the state of constant and continuous exchange with the species present in the aqueous bulk phase and thus maintaining the state of dynamic equilibrium. The hydroxyl ion in such a case will be in more favourable environment to react with the carbonium ions, resulting in the observed catalysis. The increase in anion concentration

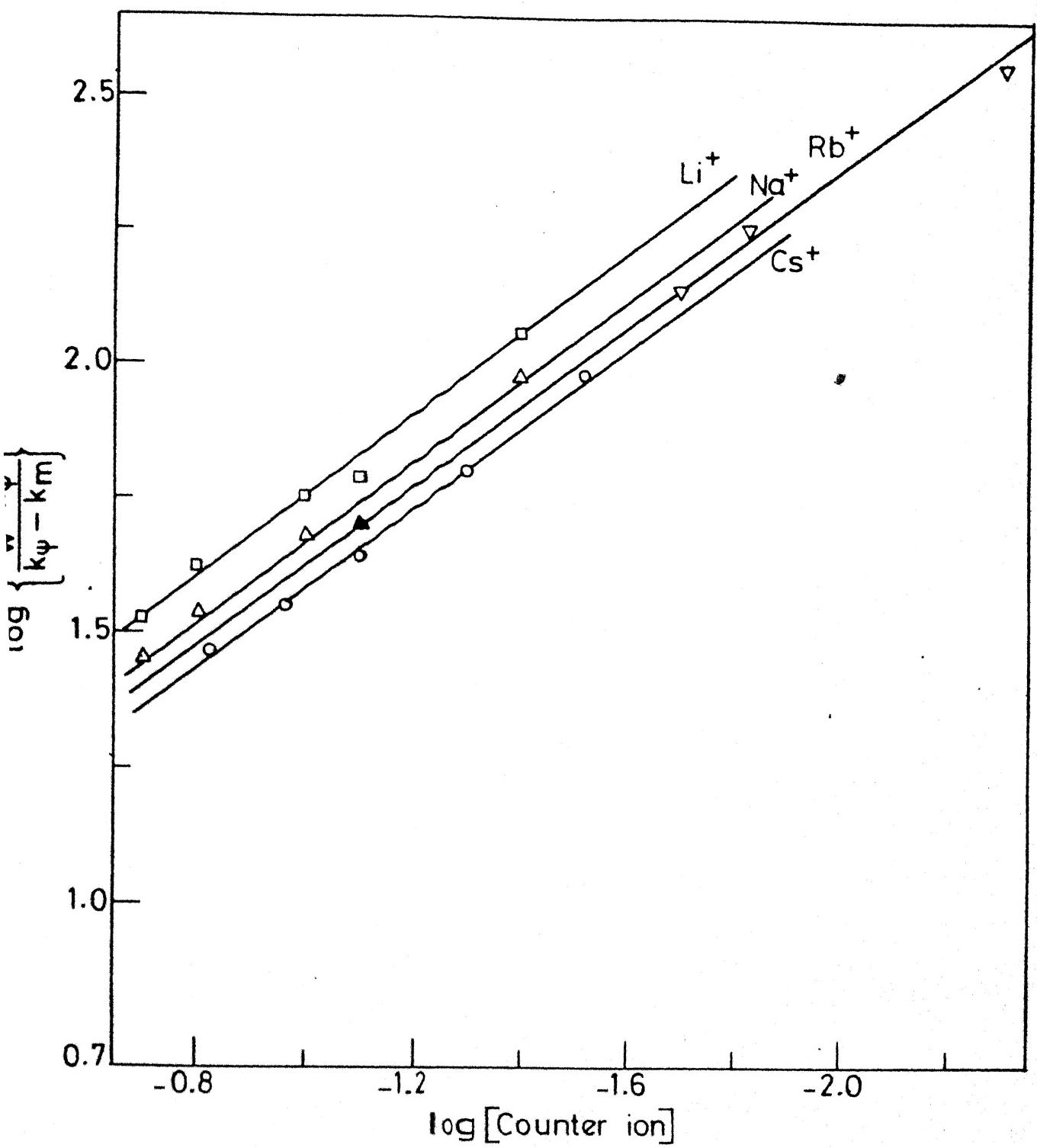


Fig. IV.7 Analysis of the effect of counter ions on the reaction of BG^+ carbonium ion with hydroxyl ion in presence of SDS (pre)micelles according to Eqn. (2.8) at 25°C .

Table IV.3. Quantitative analysis of the effect of counter ions on SDS inhibited alkaline fading reaction of tri-phenylmethyl carbonium ions at 25°C on the basis of Scheme IV.1.

Sl. No.	Counter Ion	No. (s) Analogous to Cooperativity Index		Binding Constant, K_{b1}
		n for SDS	p for Cation	

Reaction of BG^+ Carbonium Ion

$$[\text{OH}^-] = 0.010 \text{ M}$$

1.	Li^+	0.50	8.90×10^7
2.	Na^+	1.30	9.21×10^7
3.	Cs^+	0.90	5.99×10^8

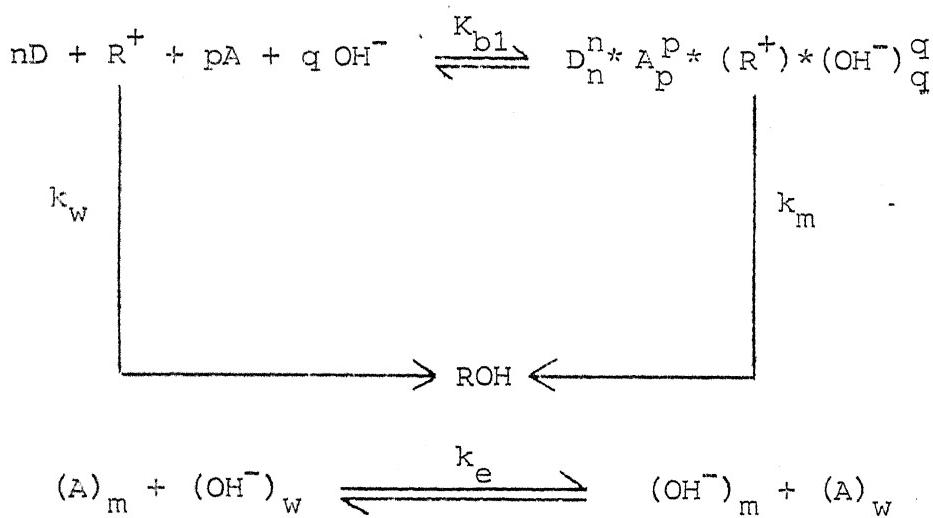
Reaction of MG^+ Carbonium Ion

$$[\text{OH}^-] = 0.010 \text{ M}$$

1.	Li^+	0.40	2.12×10^6
2.	Na^+	1.18	8.24×10^6
3.	Cs^+	0.90	4.79×10^7

in the reaction system will have the effect of reducing the reactant hydroxyl ion concentration in the vicinity of the micelles and vice versa. Thus the micellar catalysis of alkaline fading reactions of SG^+ , BG^+ and MG^+ in presence of CTAB confirms to Scheme II.2 described in Chapter II and it is shown below.^{18,19} (Scheme IV.2):

Scheme IV.2



In this reaction scheme K_{b2} is equilibrium binding constant of the substrate, R^+ , with CTAB, represented by D , in presence of counter ion, A , and hydroxyl ion. K_e is an ion exchange constant governing the concentrations of counter ion and the reactant in the vicinity of catalytic aggregates in relation to their concentrations in the bulk of the solution. All other symbols used in this reaction scheme have the same meaning as in Scheme IV.1. According to Scheme II.2 described in Chapter II the equation for the observed first order rate constant, k_ψ , may be written as

follows:

$$\frac{k_{\psi}}{k_w} = \frac{f \cdot K_e \cdot p \cdot C_R +}{C_A} \left[\frac{\frac{K_{b2} (C_D)^n (C_A)^p (C_{OH^-})^q}{1 + K_{b2} (C_D)^n (C_A)^p (C_{OH^-})^q}}{1 + K_{b2} (C_D)^n (C_A)^p (C_{OH^-})^q} \right]^2 + \frac{1}{1 + K_{b2} (C_D)^n (C_A)^p (C_{OH^-})^q} \quad \dots \quad (4.4)$$

The 'f' in Equation (2.21) is a factor by which bimolecular rate constant of the reaction of carbonium ions viz., SG^+ , BG^+ and MG^+ , with hydroxyl ion is altered in the micellar environment of CTAB, in comparison to the value of bimolecular rate constant in the absence of detergent in aqueous medium.

The method of analysis described in Chapter II for Scheme II.2 was followed to determine the values of n, p, $f \cdot K_e$ and K_{b2} corresponding to various counter ions in presence of CTAB for the reaction of carbonium ions viz., SG^+ , BG^+ and MG^+ with hydroxyl ion. These values are summarized in Table IV.4. In Figs. IV.2, IV.3 and IV.4 the theoretically generated plots of rate constant, k_{ψ} , vs counter ion concentration are shown along with the experimental points for corresponding anions for the alkaline fading reaction of SG^+ , BG^+ and MG^+ respectively in presence of CTAB. It was found that the theoretically generated curves, according to Equation 4.4, match with that of experimental one's within the range of ± 10 per cent error.

It may be noted from the results of analysis of kinetic data for micellar effects in presence of CTAB, summarized in Table IV.4,

Table IV.4. Analysis of the effects of counter-ions on CTAB (pre)micelle-catalysed reactions of triphenyl-carbonium ions with hydroxyl ion at 25°C

Sl. No.	Counter ion	No. (s) Analogous to Cooperativity Index	Factor f.K _e		Binding constant, K _{b2}
			n	p	
<u>Reaction of SG⁺ Carbonium Ion</u>					
1.	Cl ⁻		1.13	1.96×10^4	3.52×10^3
2.	Br ⁻		1.45	1.92×10^4	9.97×10^3
3.	N ₃ ⁻	3.05	1.49	1.80×10^4	2.64×10^4
4.	NO ₃ ⁻			1.54×10^4	1.48×10^4
<u>Reaction of BG⁺ Carbonium Ion</u>					
1.	Ac ⁻		0.16	1.72×10^4	5.12×10^2
2.	Cl ⁻		0.76	1.47×10^4	6.40×10^2
3.	NO ₃ ⁻	2.17	0.76	1.37×10^4	7.54×10^2
4.	Br ⁻		0.77	1.16×10^4	7.89×10^3
<u>Reaction of MG⁺ Carbonium Ion</u>					
1.	Cl ⁻		0.37	6.95×10^3	5.93×10^2
2.	NO ₃ ⁻	2.40	0.37	5.64×10^3	1.41×10^3
3.	Br ⁻		0.48	3.33×10^3	1.12×10^3

that the values of K_{b2} and p increase whereas the relative values of $f \cdot K_e$ decrease with increasing size and low charge density of the anions.

IV.5 DISCUSSION

The analysis of micellar data for the reaction of carbonium ions viz., SG^+ , BG^+ and MG^+ with hydroxyl ion on the basis of Equations 4.1 and 4.2 gave excellent straight line plot (Fig. IV.6) which demonstrates the validity of the formulation and applicability of model shown in Scheme IV.1 for these reactions. The relative increase in the values of p and K_{b1} in presence of various counter ions in the order of their position in the lyotropic series (Table IV.3) indicates that the counter ions do interact with the catalytic micelles and the interaction is stronger for large sized and low charge density ions.

The effect of counter ions on the inhibition caused by the presence of SDS in the reaction system was studied in the range of concentration of detergent which corresponded to the saturation concentration in the rate vs surfactant concentration profile. Thus the replacement of the substrate, for which favourable electrostatic as well as hydrophobic interactions with the detergent exist, by hydrophilic cations is not possible. The concentration range in which the counter ion effects on these reactions in presence of SDS was examined was low enough to cause any changes in the aggregational properties of the detergent. Consequently, the contributions to the observed counter ion effects due to these

factors are ruled out. Thus, the neutralization of the surface charges of the catalytic micelles and the alteration in the thermodynamic parameters of the reactions seem to be the factors responsible for the observed micellar effects. The results that no counter ion effects are observed in case of reaction of SG^+ carbonium ion with hydroxyl ion in presence of SDS, which was studied at relatively higher reactant concentration, confirm this thesis. At high hydroxide concentration the sodium ions furnished by sodium hydroxide would neutralize almost completely the charges of the heads groups of catalytic micelles and a further addition of counter ion does not cause any change in the organization of catalytic micelles. Therefore, no effect was recorded as a function of increasing counter ion concentration on this reaction in presence of SDS.

The effect of SDS on the alkaline fading reaction of SG^+ , BG^+ and MG^+ carbonium ions is explainable on the basis of the stabilization of ground state of the reaction with respect to transition state, as a result of complexation of the substrate in presence of micelle-forming surfactant, and the non-approachability of reactant hydroxyl ion to the negatively charged catalytic micelles. The addition of counter ions to the reaction system results in the neutralization of the surface charges of the catalytic aggregates which in turn would destabilize the ground state of the reaction with respect to transition state as compared to situation when no counter ions were present in the reaction system. Further, this neutralization would relatively facilitate the

approach of reactant hydroxyl ion to the complexed carbonium ion resulting in the increased rate with increasing concentration of the counter ions. Therefore, the neutralization of the charges on the catalytic micelles and the changes in the thermodynamic parameters of the reaction in presence of detergent and the salts are responsible factors for the observed micellar effects in presence of SDS.

In case of the reaction of carbonium ions in presence of CTAB analyzed on the basis of Scheme IV.2 the values of p , corresponding to cooperativity index of anions, and k_{b2} , the equilibrium binding constant increase whereas the value of $f \cdot K_e$ decreases with increasing size and low charge density of counter ions. The trend in values of p and K_{b2} corresponding to various anions demonstrate that the counter ions do participate in the formation of catalytic micelles. The interaction of counter ions with the catalytic micelles will have the effect of neutralization of charges possessed by the head groups. Consequently, the ground state of the reaction will be relatively stabilized as compared to transition state of the reaction. This comparison is made in relation to the situation when no counter ions are present in the reaction system. The decrease in the value of ion exchange equilibrium constant, K_e , with ions of increasing size and low charge density, according to Scheme IV.2, indicates the lowering of hydroxyl ion concentration in the vicinity of catalytic micelles.

It may be pointed out that the addition of counter ions neutralizes the surface charges of catalytic micelles which in

turn stabilizes the ground state of the reaction with respect to transition state compared to the situation when no added counter ions are present in the reaction system. In such a situation the value of f would decrease with respect to its value in the absence of any of the added counter ions at the same detergent concentration. Thus the values of f as well as K_e and therefore the value of the product $f \cdot K_e$ should decrease with the increasing effectiveness of the counter ions in changing the extent of micellar catalysis in these reactions.

The effect of counter ions on micellar catalysis can not necessarily be attributed to the replacement of the substrate from complexed phase to the aqueous bulk phase because the effect of counter ions in these reaction was studied at a concentration of CTAB which was much higher than the saturation concentration of the detergent in rate vs surfactant concentration profile ($F_m \rightarrow 1$). Further the neutralization of the head groups charges by counter ion would reduce the unfavourable electrostatic interaction and thus would enhance the binding between the substrate and the detergent. The contribution due to changes in the aggregational properties of CTAB as a result of the addition of salts to reaction system may be considered insignificant since the concentration of these salts in not varied to high concentrations.

It is proper to mention here that (i) the values of n , corresponding to cooperativity index of the detergent, are different for the reaction of various substrates viz., SG^+ , BG^+ and IG^+ carbonium ion with reactant hydroxyl ion in presence of the

same surfactant, CTAB. (ii) The values of p for various anions in presence of CTAB corresponding to any of the considered reactions are different; and (iii) The values of p for the same counter ions in different reaction systems viz., alkaline fading reaction of SG^+ , BG^+ and SG^+ carbonium ions, in presence of CTAB are different. These results clearly indicate that the composition of catalytic micelles formed by the participation of various substrates in the micellar environment are different and that the degree of ionization of catalytic micelles in presence of several counter ions may not be constant.

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CHAPTER V

MICELLAR EFFECT ON THE REACTION
OF TRIPHENYLMETHYL CARBONIUM IONS
WITH HYDROXYL ION : INFLUENCE OF
ORGANIC SOLVENTS AND TEMPERATURE

V.1 ABSTRACT

A general background is presented for the analysis and interpretation of micellar data for the effect of organic solvents on chemical reactions in view of the current thinking of the effect of organic solvents on chemical reactivity in solution i.e., the effect of selective solvation and the accompanying motion of solvent molecules along with the reactants along the reaction coordinates at the transition state. It is pointed out that effect of organic solvents on chemical reactions in presence of micelle-forming surfactants involve competing as well as compensating phenomenon. Thus either enhancement or the retardation may result in the reaction rate upon the addition of organic solvents to reaction system containing micelle-forming surfactant.

The effect of various organic solvents on the reaction of SG^+ , RG^+ and MG^+ carbonium ions with hydroxyl ion in presence of SDS and CTAB is reported. The values of activation parameters for these reactions in absence of surfactant, in presence micellar environment of CTAB and also that of SDS have been evaluated. It is pointed out that the values of ΔS^\ddagger and Z calculated in presence of SDS correspond to lower limits and the values of these quantities calculated in presence of CTAB correspond to upper limits of these parameters. The values of ΔF^\ddagger in SDS and in CTAB correspond to upper and lower limits, respectively.

V.2 INTRODUCTION

In the past few decades advances have been made in the field of chemical kinetics to such an extent that mechanistic

descriptions of many chemical reactions can be given in molecular terms. As a consequence of very impressive amount of work carried out in homogeneous medium the theories of reaction mechanism have provided considerable predictive power.¹⁻⁴ However, the ideas concerning solvent effects on reactivity have undergone drastic amendments since the proposal of the classical concept of solvent as a continuous dielectric medium.⁵⁻⁹ In spite of many recently proposed theories to explain effect of solvents on reactivities in solution, which focus attention on some particular aspects of solvents such as ionizing power, viscosity, dipolar association or hydrogen bonding ability etc., there has been need of radical change to explain effect of solvents on chemical reactivity.¹⁰⁻¹⁵ Evidences have been accumulating over the years which indicate that the selective solvation of reactants and the motion of solvent molecules constitutes an important and integral part of motion of the reacting species along the reaction coordinates at the transition state.¹⁴⁻¹⁹ This state of affairs is particularly true for ionic reactions. As a result of accompanying motion of solvent molecules the energy required to remove a solvent molecule from a reactive site to make space for an approaching reactant, or to reorganize the solvent molecules as a function of the change in charge distribution, may have a significant contribution to the activation energy in many reactions.¹⁵ Further, investigations have confirmed the following: (i) that the energy associated with solvation is often large, especially for ions, (ii) that the solvation energy can be a major factor influencing the

transition state parameters and thus the reaction rates, (iii) that this solvation energy varies considerably from one solvent to another, (iv) that interactions of solutes with solvents are often specific, not simply electrostatic and (v) that the effect of a solvent on various chemical reactions is distinct and different.

It has been pointed out in Chapter I that the presence of micelle-forming surfactant in the reaction system has the effect of forming catalytically functional aggregates involving substrate, detergent, additive and/or the reactant species. In this process the activation parameters of the reaction and the concentration of reactants at the reaction sites in micellar environment are modified. Following the concept that micelles in aqueous medium, formed as a result of association of pure surfactant entities, may be modified in structure or destroyed finally by the addition of organic additives to the micellar system, it may be argued that the addition of organic solvents to a reaction system containing catalytic micelles may result in the alteration of the composition and/or ultimate destruction of these catalytic aggregates.

In view of the preceding discussion it may be concluded that the overall effect of solvents on reaction rate in presence of micelle-forming surfactant, involve competitive as well as compensative phenomenon. Thus the addition of organic solvents to reaction system, containing micelle-forming surfactant, may result in either retardation or enhancement of the micellar

effects on the reaction rate.

Effect of organic solvents on chemical reactions in the micellar environment is relatively an unexplored area. One of the paramount tasks before attempting to distinguish among various factors, which control the effect of organic solvents on reaction rates, in presence of micelle-forming surfactants, is careful collection of experimental data for these effects. Since the perturbation of activation parameters of chemical reactions is the common feature of both micellar as well as that of solvent effects, the evaluation of these parameters in presence of solvents and also in micellar environment seems to be an utmost necessity for the meaningful interpretation of solvent effects on chemical reactions, in presence of micelle-forming surfactants.

Bunton and Robinson²² have studied cetyltrimethylammonium bromide (CTAB) catalysed reaction of 2,4-dinitrochlorobenzene with hydroxyl ion in ethanol-water and a t-butanol-water mixtures. Further studies on the effect of organic solvents on this reaction in presence of CTAB were carried out by Blandamer and Reid.²³ Dunlop and Cordes²⁴ have reported the effect of concentration of monohydric alcohols viz., ethanol, 1-butanol and 1-heptanol and that of dimethyldodecyl phosphine on the acidic hydrolysis of methyl orthobenzoate in presence of sodium dodecyl sulfate (SDS). Applicability of Arrhenius equation and the evaluation of activation parameter for chemical reactions is also reported in the literature.²⁷⁻³³

In this chapter the effect of organic solvents on the reaction of triphenylmethyl carbonium ions viz., setoglaucine (SG^+), brilliant green (BG^+) and malachite green (MG^+) with hydroxyl ion in presence of SDS as well as that of CTAB is reported. The thermodynamic activation parameters for these reactions in aqueous medium and also in various solvent-water mixtures are available in the literature.^{19,21} The values of these parameters in presence of CTAB and SDS for these reactions have also been evaluated and are being reported here.

V.3 EXPERIMENTAL SECTION

V.3.1 Method

All the studies were performed at $25 \pm 0.1^\circ\text{C}$ following the procedure described in Chapter III.

V.3.2 Reagents

The solvents viz., acetone, ethanol, n-propanol, n-butanol, n-hexane and ethylene glycol were BDH AnalaR grade chemicals and were purified further before use following the standard procedures described in literature.³⁴ Purity of other chemicals used in these studies was as described earlier.

V.4 RESULTS

V.4.1 Effect of Organic Solvents on SDS Inhibited Reaction of Triphenylmethyl Carbonium Ions with Hydroxyl Ion

The influence of organic solvents on the SDS inhibited reaction of triphenylmethyl carbonium ions viz., SG^+ , BG^+ and

MG^+ was examined at fixed concentrations of detergent, reactant and substrate by varying the concentrations of organic solvents in the reaction system. The studies were performed at concentration of SDS which corresponded to saturation concentration in the rate vs surfactant concentration profile.

a. Alkaline fading reaction of SG^+ carbonium ion- The effect of organic solvents viz., acetone, ethanol, n-propanol and n-butanol on the SDS inhibited alkaline fading reaction of SG^+ carbonium ion was studied by adding varying amount of organic solvent in the reaction system at fixed concentrations of surfactant (0.005M), substrate (1.2×10^{-5} M) and reactant hydroxyl ion (0.20 M). It may be noted from the kinetic data summarized in Table V.1 that the increasing amount of solvent reduces the overall inhibition of the reaction caused by the presence of SDS in the reaction system.

b. Alkaline fading reaction of BG^+ carbonium ion- The effect of various organic solvents viz., acetone, ethanol, n-propanol, n-butanol, dioxane and ethylene glycol was examined on the reaction of BG^+ carbonium ion with hydroxyl ion by keeping the concentrations of SDS (0.005 M), reactant (0.005M) and substrate (1.2×10^{-5} M) fixed and varying the solvent percentage in the reaction system. The values of rate constant as a function of the concentration of organic solvents in the reaction system are summarized in Table V.1. The effect is also shown in Fig. V.1.

c. Alkaline fading reaction of MG^+ carbonium ion- The investigation

Table V.1. The values of pseudo first order rate constant for the effect of organic solvents on the SDS inhibited alkaline fading reaction of SG⁺, BG⁺ and MG⁺ carbonium ions at 25°C.

$$[\text{SDS}] = 0.005 \text{ M}; [\text{Substrate}] = 1.2 \times 10^{-5} \text{ M}$$

Sl. No.	Solvent (%)	First order rate constant $k\psi \times 10^2 \text{ min}^{-1}$, for the fading reaction of carbonium ions.		
		SG ⁺ $[\text{OH}^-] = 0.2 \text{ M}$	BG ⁺ $[\text{OH}^-] = 0.005 \text{ M}$	MG ⁺ $[\text{OH}^-] = 0.01 \text{ M}$
1	2	3	4	5
<u>Acetone</u>				
1.	0	1.07	0.36	1.01
2.	2		0.43	1.33
3.	2.5	1.60		
4.	4.0		0.55	1.69
5.	5.0	2.13		
6.	6.0		0.73	2.21
7.	7.5	2.53		
8.	8.0		1.14	3.13
9.	10.0	3.28	3.01	5.20
10.	12.5	3.09		
11.	15.0	5.70		
12.	20.0	12.89		
<u>Ethanol</u>				
1.	1.0	1.32		
2.	2.0	1.50	0.44	1.24
3.	3.0	1.78		
4.	4.0	3.22	0.53	1.35
5.	5.0	3.34		
6.	6.0		0.67	1.83
7.	8.0	0	0.86	1.96
8.	10.0	4.38	1.11	2.30
9.	12.5			
10.	15.0	9.56		
11.	20.0	13.82		

contd...

Table V.1 (contd.)

1	2	3	4	5
<u>n-Propanol</u>				
1.	2.0	1.90	0.52	1.30
2.	4.0	2.59	0.80	1.63
3.	6.0	4.15	1.10	2.28
4.	8.0		1.74	3.29
5.	10.0	9.05	2.80	5.07
6.	15.0	28.78		
<u>n-Butanol</u>				
1.	0.5	1.61		
2.	1.0	2.13	0.84	1.56
3.	1.5		1.36	2.16
4.	2.0	3.51	2.41	2.63
5.	3.0	5.64		4.53
6.	4.0		3.93	7.74
7.	5.0	12.23	6.75	
<u>Dioxane</u>				
1.	2.0		0.50	1.25
2.	4.0		0.65	1.54
3.	6.0		0.83	1.90
4.	8.0		1.06	2.58
5.	10.0		1.54	4.49
<u>Ethylene Glycol</u>				
1.	2.0		0.40	1.37
2.	4.0		0.45	1.69
3.	6.0		0.61	2.08
4.	8.0		0.74	2.29
5.	10.0		0.98	2.88

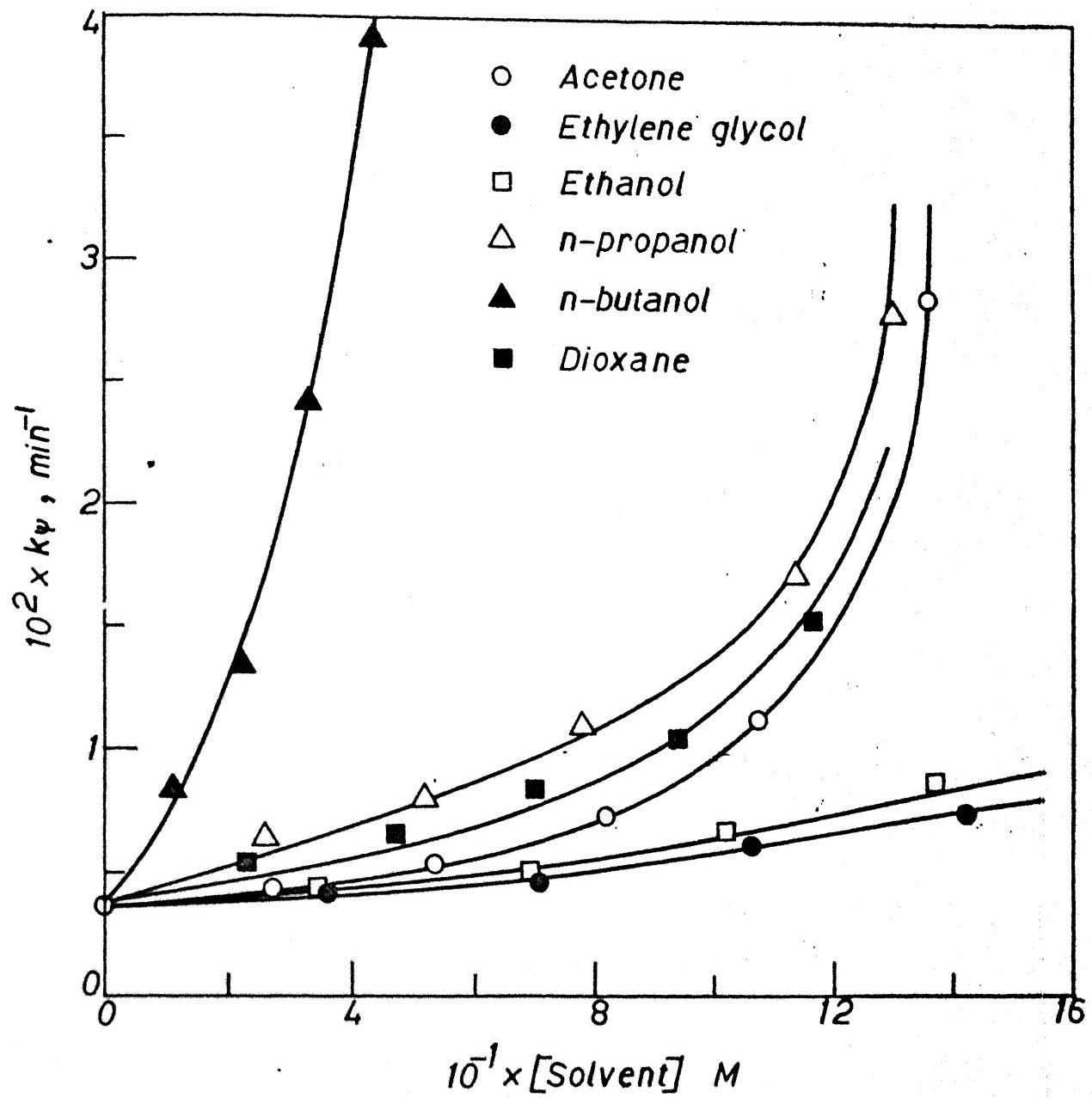
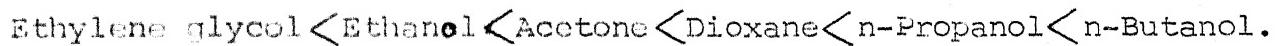


Fig. V.1 Variation of pseudo first order rate constant as a function of added organic solvent concentration on SDS inhibited alkaline fading reaction of BG^+ Carbonium ion with hydroxyl ion at 25°C .

on the effect of organic solvents on the reaction of MG^+ carbonium ion with hydroxyl ion in presence of SDS was done at fixed concentration of detergent (0.005 M), reactant (0.01 M) and the substrate (1.2×10^{-5} M) by varying concentration of various solvents in the reaction system. The kinetic data for this effect are summarized in Table V.1 and also exhibited in Fig. V.2.

d. General features of the effect of organic solvents on SDS inhibited alkaline fading reaction of triphenylmethyl carbonium ions-

It may be observed from the kinetic data recorded in Table V.1 and Figs. V.1 and V.2 that the increasing concentration of organic solvents in the reaction system containing SDS results in the marked reduction of overall micellar inhibition of these reactions. Further, the effectiveness of alcohols increases with the increasing carbon chain length of the molecules. The capability of solvents to decrease the micellar inhibition of these reactions in presence of SDS was found in the following increasing order:



v.4.3 Effect of Organic Solvents on CTAB Catalysed Reaction of Triphenylmethyl Carbonium Ion with Hydroxyl Ion

The effect of various organic solvents viz., ethanol, n-propanol, acetone, and ethylene glycol on the CTAB catalysed alkaline fading reaction of SG^+ , BG^+ and MG^+ carbonium ions was investigated by keeping the concentrations of detergent, reactant and the substrate constant and varying solvent concentration in

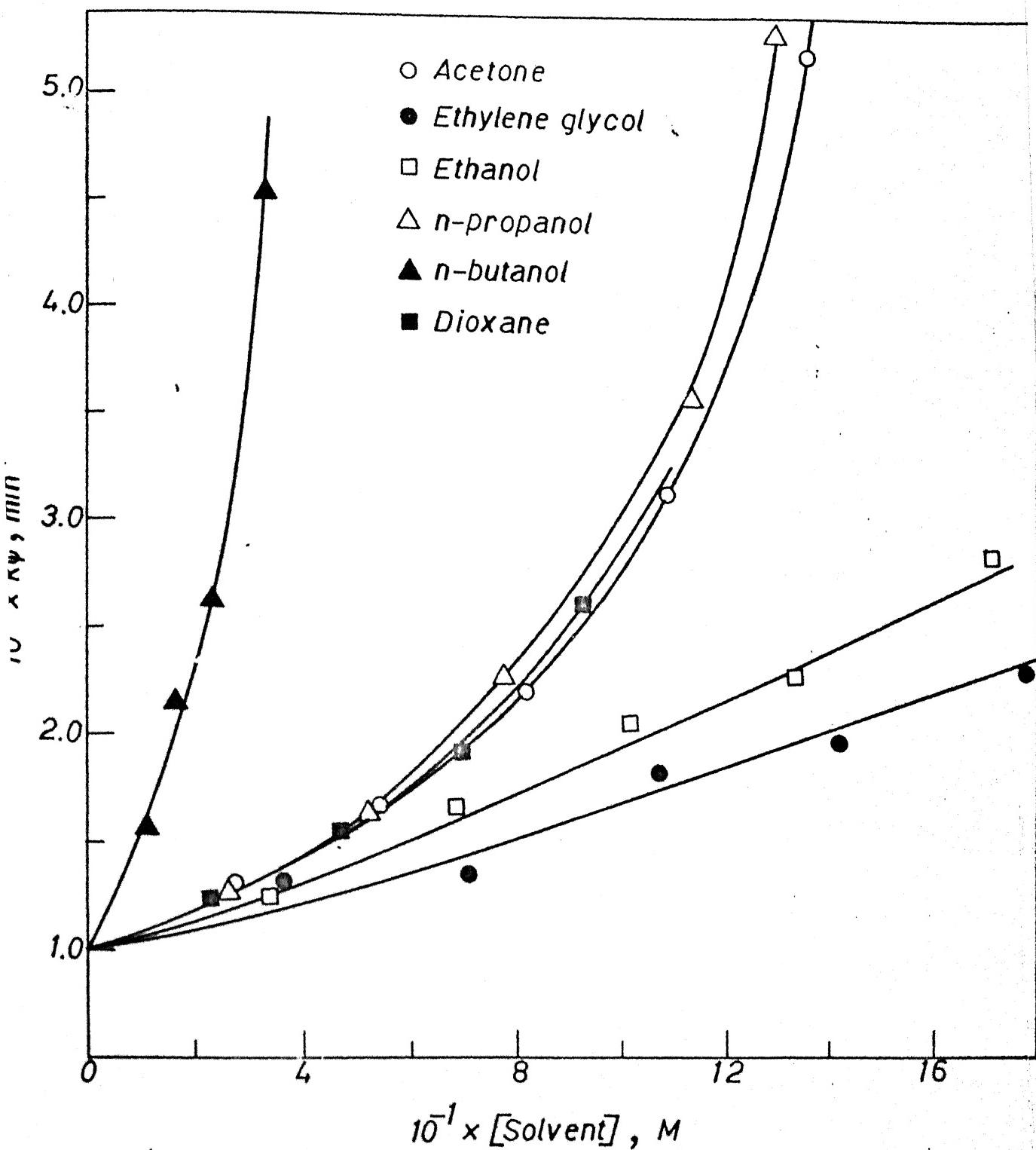


Fig. VII.2 The effect of organic solvents on the alkaline fading reaction of MG^+ Carbonium ion in presence of SDS at 25°C .

the reaction system. The concentration of the detergent was selected such that it corresponded to the saturation concentration of CTAB in the rate vs surfactant concentration profile for these reactions.

a. Reaction of SG⁺ carbonium ion with hydroxyl ion- The effect of organic solvents viz., acetone, ethanol, n-propanol and ethylene glycol on the alkaline fading reaction of SG⁺ carbonium ion in presence of CTAB was studied at fixed concentrations of detergent (0.02 M), substrate (1.8×10^{-5} M) and the reactant. The hydroxyl ion concentration for the investigation on the effects of acetone, ethanol and n-propanol was kept 0.01 M and for the effect of ethylene glycol was maintained 0.001 M. The kinetic data for these effects are summarized in Table V.2 and are also shown in Fig. V.3.

b. Reaction of BG⁺ carbonium ion with hydroxyl ion- The studies of the effect of organic solvents on the alkaline fading reaction of BG⁺ carbonium in presence of CTAB were carried out at fixed concentrations of detergent (0.02 M), substrate (1.8×10^{-5} M) and the hydroxyl ion. The hydroxyl ion concentration was kept 0.001M in case of acetone and n-propyl alcohol and 0.0005 M in case of ethyl alcohol. The values of first order rate constant for the effect described, are summarized in Table V.2.

c. Reaction of MG⁺ carbonium ion with hydroxyl ion- The effect of organic solvents viz., acetone, ethyl alcohol and ethylene glycol on the reaction of MG⁺ carbonium ion and hydroxyl ion was

Table V.2. Effect of organic solvents on the alkaline fading reaction of SG⁺, BG⁺ and MG⁺ carbonium ions in presence of CTAB at 25°C.

$$[\text{CTAB}] = 0.02 \text{ M}; [\text{Substrate}] = 1.8 \times 10^{-5} \text{ M}$$

Sl. No.	Solvent % (v/v)	First order rate constant, $k_{\text{pH}} \times 10^2 \text{ min}^{-1}$, for the reaction of carbonium ions		
		SG ⁺	BG ⁺	MG ⁺
1	2	3	4	5
<u>Acetone</u>				
		$[\text{OH}^-] = 0.01 \text{ M}$	$[\text{OH}^-] = 0.001 \text{ M}$	$[\text{OH}^-] = 0.001 \text{ M}$
1.	0	1.5	13.44	8.69
2.	2.0		12.56	
3.	2.5	0.88		7.24
4.	4.0		9.84	
5.	5.0	0.61		4.68
6.	6.0		77.52	
7.	7.5	0.42		3.06
8.	8.0		6.79	
9.	10.0	0.31	5.72	2.49
10.	12.5	0.23		
11.	15.0	0.17		1.61
12.	17.5	0.13		
13.	20.0	0.10		

<u>Ethanol</u>				
		$[\text{OH}^-] = 0.01 \text{ M}$	$[\text{OH}^-] = 0.0005 \text{ M}$	$[\text{OH}^-] = 0.0002 \text{ M}$
1.	0	1.152	13.44	4.42
2.	2.0		13.47	3.87

.....contd.

Table V.2 (contd.)

1	2	3	4	5
3.	2.5	1.113		
4.	4.0		13.34	2.83
5.	5.0	1.005		
6.	6.0		13.41	2.04
7.	7.5	0.933		
8.	8.0		13.31	1.45
9.	10.0	0.800	11.17	1.31
10.	12.5	0.674		
11.	15.0	0.514		
12.	17.5	0.451		
13.	20.0	0.397		

n-Propanol

$$[\text{OH}^-] = 0.01 \text{ M} \quad [\text{OH}^-] = 0.001 \text{ M}$$

1.	0	1.152	13.44
2.	2.0		13.54
3.	2.5	0.829	
4.	4.0		12.80
5.	5.0	0.507	
6.	6.0		11.29
7.	7.5	0.421	
8.	8.0		8.45
9.	10.0	0.317	7.79

...contd.

Table V.2 (contd.)

1	2	3	4	5
10.	12.5	0.245		
11.	15.0	0.157		
12.	20.0	0.259		

Ethylene Glycol

$$[\text{OH}^-] = 0.001 \text{ M} \quad [\text{OH}^-] = 0.0002 \text{ M} \quad [\text{OH}^-] = 0.0001 \text{ M}$$

1.	0	1.975	-	2.20
2.	1.0	2.390		2.46
3.	2.0	2.965		2.72
4.	3.0	3.050		3.87
5.	4.0	3.715		5.01
6.	5.0	4.944		5.93
7.	7.0			5.15
8.	7.5	4.567		
9.	8.5	3.253		
10.	10.0	3.368		3.38
11.	15.0	3.023		
12.	20.0	2.706		

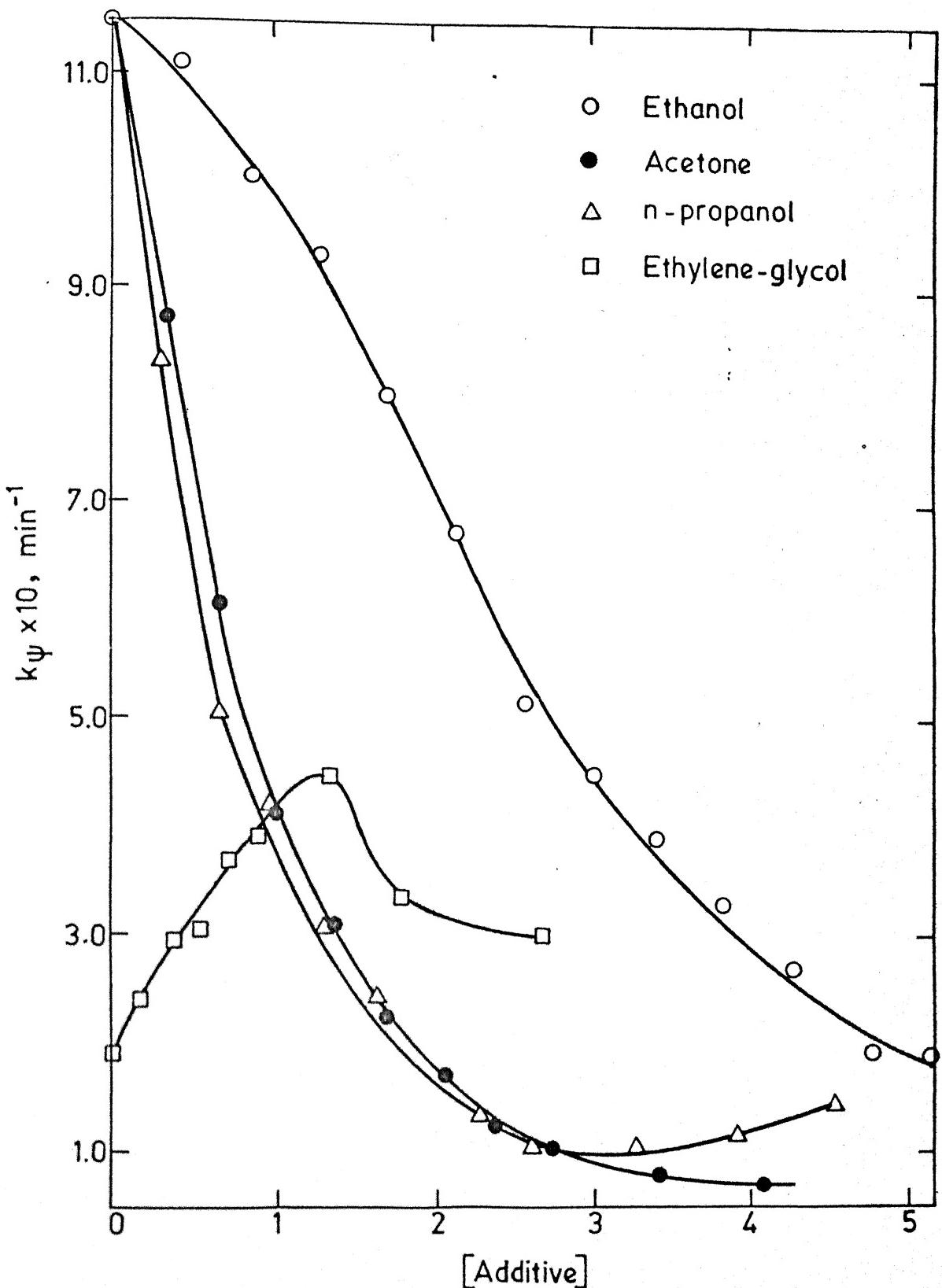


Fig. VII.3 Solvents effect on micellar catalysis of CTAB on the reaction of SG⁺, BG⁺, and MG⁺ carbonium ions with hydroxyl ion at 25°C.

investigated at fixed concentration of CTAB (0.02 M), substrate (1.8×10^{-5} M) and the reactant. The concentration of hydroxyl ion was maintained 0.0002 M for ethanol, 0.001 M for acetone and 0.0001 M for ethylene glycol. The values of rate constant in presence of various concentration of organic solvents are summarized in Table V.2 and also shown in Fig. V.4.

d. General features of the effect of organic solvents on CTAB catalysed alkaline fading reactions of triphenylmethyl carbonium ion-

It may be noted from the data summarized in Table V.2 and also shown in Fig. V.3 and V.4 that ethyl alcohol, n-propyl alcohol and acetone have the effect of reducing the micellar catalysis of the reaction of triphenylmethyl carbonium ions with hydroxyl ion caused by the presence of CTAB in the reaction system. Propyl alcohol is more effective in reducing the overall catalysis of these reactions as compared to that of ethyl alcohol. Ethylene glycol exhibits anomalous effect e.g., increasing concentration of ethylene glycol in the reaction system in the beginning results in the enhancement of the catalysis and a further increase in the concentration of this solvent has the effect of diminishing the value of rate constant after passing through a maximum value.

V.4.3 Effect of Temperature on SDS Inhibited Reaction of Triphenylmethyl Carbonium Ions with Hydroxyl Ion

In order to obtain the values of activation parameters of the reaction of triphenylmethyl carbonium ions with hydroxyl ion

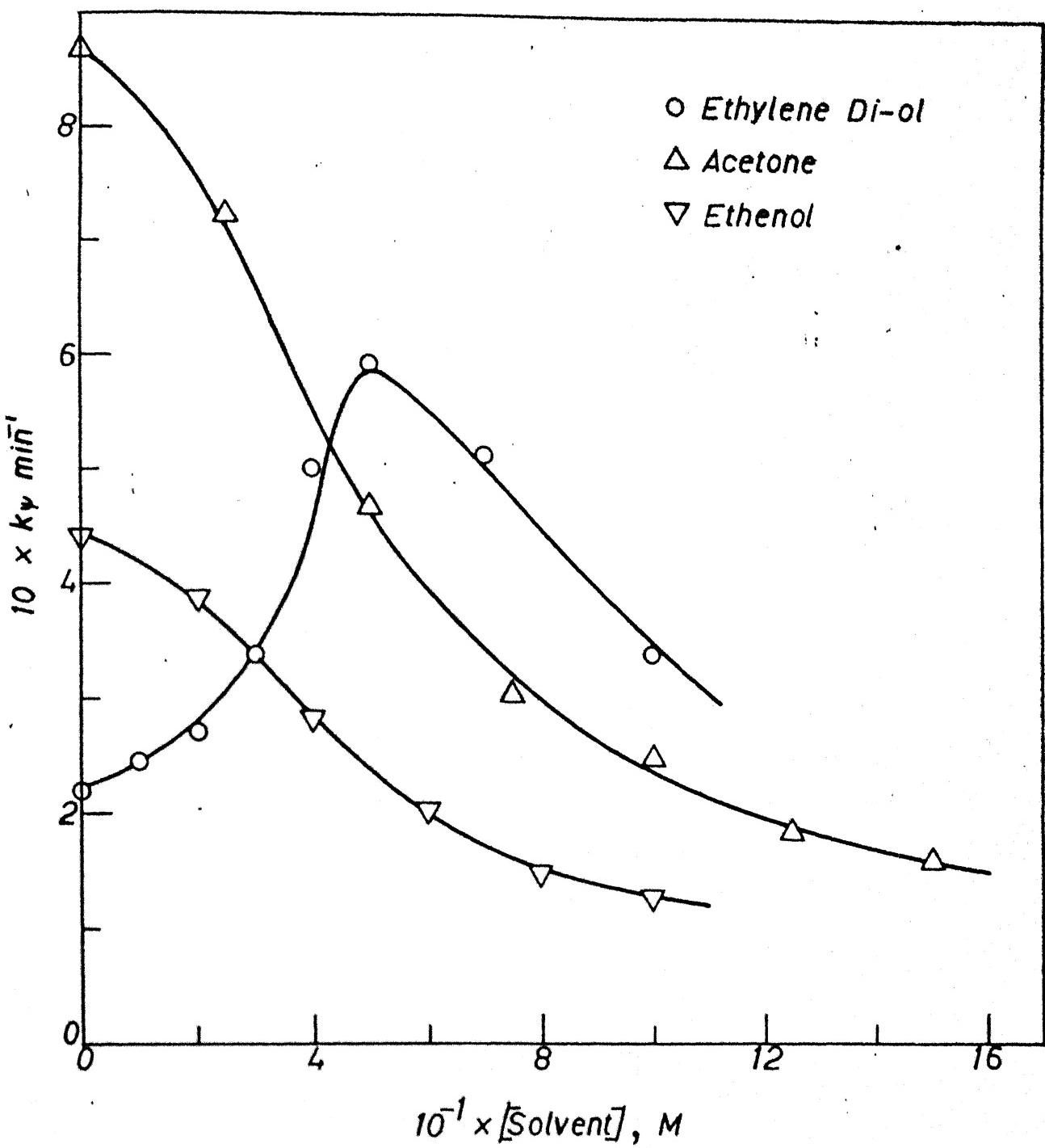


Fig. VII:4 The effect of organic solvents on the micellar catalysis of CTAB for the alkaline fading reaction of MG^+ Carbonium ion at 25°C .

in the micellar environment the effect of temperature on these reactions was studied. The investigations were carried out by determining the values of rate constant at different temperatures at fixed concentrations of detergent, substrate and the reactant.

a. Reaction of SG⁺ carbonium ion with hydroxyl ion- The effect of temperature on the alkaline fading reaction of SG⁺ carbonium was studied by measuring the value of rate constant at 25°C, 30°C, 35°C and 40°C at fixed concentration of detergent (0.005 M), substrate (1.2×10^{-5} M) and the reactant (0.1 M). The values of rate constant at different temperatures for this reaction in presence of SDS are summarized in Table V.3.

b. Reaction of BG⁺ carbonium ion with hydroxyl ion- The effect of temperature on the alkaline fading reaction of BG⁺ carbonium ion in presence of SDS was examined at fixed concentrations of detergent (0.005 M) substrate (1.2×10^{-5} M) and the reactant (0.01 M) at four different temperatures viz., 25°C, 30°C, 35°C and 40°C. The kinetic parameters for the effect of temperature are summarized in Table V.3.

c. Reaction of MG⁺ carbonium ion with hydroxyl ion- The influence of temperature on the reaction of MG⁺ carbonium ion with hydroxyl ion in presence of SDS was investigated by finding the values of first order rate constant at four different temperatures viz., 25°C, 30°C, 35°C and 40°C at fixed concentrations of detergent (0.005 M) substrate (1.2×10^{-5} M) and the reactant

Table V.3. The values of first order rate constant as a function of temperature for the alkaline fading reaction of SG⁺, BG⁺ and MG⁺ carbonium ions.

Sl. No.	Tempe- rature	First order rate constant, min ⁻¹		
<u>In Presence of 0.02 M CTAB</u>				
		$[SG^+] = 1.8 \times 10^{-5} M$	$[BG^+] = 1.8 \times 10^{-5} M$	$[MG^+] = 1.8 \times 10^{-5} M$
		$[OH^-] = 0.001 M$	$[OH^-] = 0.0001 M$	$[OH^-] = 0.0001 M$
1.	20°C	4.54×10^{-2}	7.77×10^{-2}	1.46×10^{-2}
2.	25°C	6.04×10^{-2}	10.02×10^{-2}	3.33×10^{-2}
3.	30°C	8.03×10^{-2}	12.82×10^{-2}	4.51×10^{-2}
4.	35°C	10.67×10^{-2}	16.46×10^{-2}	6.07×10^{-2}
5.	40°C			8.05×10^{-2}
<u>In Absence of Surfactant</u>				
		$[SG^+] = 1.4 \times 10^{-5} M$	$[BG^+] = 1.4 \times 10^{-5} M$	$[MG^+] = 1.4 \times 10^{-5} M$
		$[OH^-] = 0.01 M$	$[OH^-] = 0.002 M$	$[OH^-] = 0.001 M$
1.	20°C	3.21×10^{-2}		
2.	25°C	4.61×10^{-2}	5.86×10^{-2}	6.47×10^{-2}
3.	30°C	6.63×10^{-2}	11.92×10^{-2}	9.61×10^{-2}
4.	35°C	9.49×10^{-2}	16.82×10^{-2}	14.26×10^{-2}
5.	40°C	13.18×10^{-2}	23.06×10^{-2}	30.45×10^{-2}
<u>In Presence of 0.005 M SDS</u>				
		$[SG^+] = 1.2 \times 10^{-5} M$	$[BG^+] = 1.2 \times 10^{-5} M$	$[MG^+] = 1.2 \times 10^{-5} M$
		$[OH^-] = 0.1 M$	$[OH^-] = 0.01 M$	$[OH^-] = 0.01 M$
1.	25°C	3.21×10^{-3}	6.60×10^{-3}	10.10×10^{-3}
2.	30°C	5.13×10^{-3}	10.34×10^{-3}	16.64×10^{-3}
3.	35°C	8.13×10^{-3}	16.09×10^{-3}	27.16×10^{-3}
4.	40°C	12.56×10^{-3}	24.40×10^{-3}	43.14×10^{-3}

(0.01 M). The values of first order rate constant at different temperatures for this reaction system are summarized in Table V.3.

d. General features of the effect of temperature on the reaction of triphenylmethyl carbonium ions with hydroxyl ion in presence of SDS- The value of the rate constant for the reaction of triphenylmethyl carbonium ions with hydroxyl ion in presence of SDS increases with increasing temperature of the reaction system. The plot of logarithm of rate constant vs inverse of absolute temperature gives straight line exhibiting the applicability of Arrhenius law for these reactions in the micellar environment of SDS. One such plot for the reaction of SG^+ carbonium ion with hydroxyl ion is shown in Fig. V.5.

V.4.4 Effect of Temperature on CTAB Catalysed Reaction of Triphenylmethyl Carbonium Ions with Hydroxyl Ion

The effect of temperature on the alkaline fading reaction of triphenylmethyl carbonium ions with hydroxyl ion was studied by recording the values of rate constant for these reactions at different temperatures at fixed concentrations of detergent substrate and the reactant. The values of rate constant for these reactions in presence of CTAB as a function of temperature are summarized in Table V.3.

a. Alkaline fading reaction of SG^+ carbonium ion- The effect of temperature on the CTAB catalysed reaction of SG^+ carbonium ion with hydroxyl ion was studied at fixed concentrations of detergent (0.02 M) substrate (1.8×10^{-5} M) and the reactant (0.001 M) by

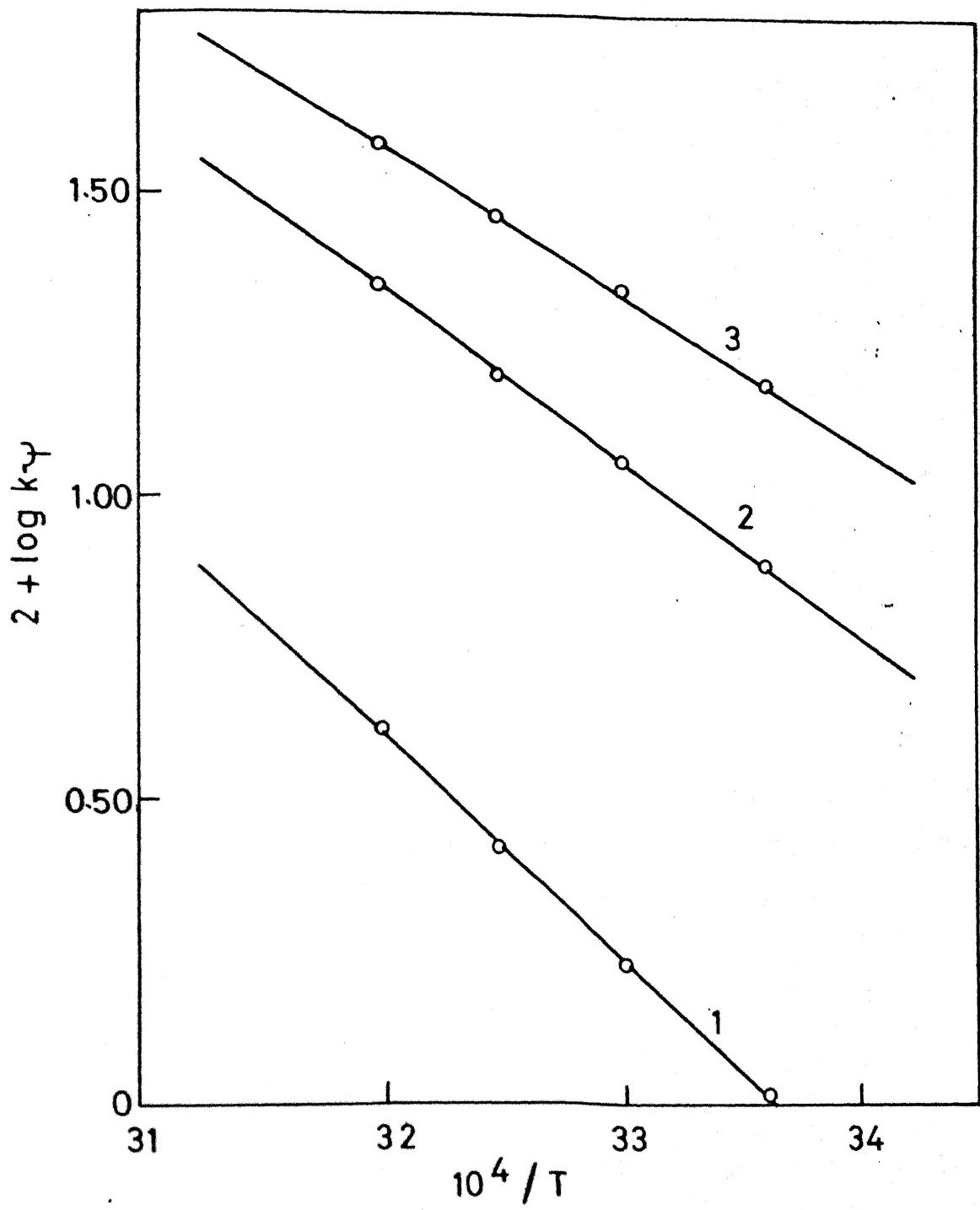


Fig. IV.5 Arrhenius plots for the reaction of SG⁺ Carbonium ion;
 plot 1, in presence of 0.005M SDS and 0.1M NaOH;
 plot 2, in presence of 0.01M NaOH and plot 3, in presence
 of 0.02M CTAB and 0.001M NaOH solutions.

recording the values of first order rate constant at different temperatures viz., 20°C, 25°C, 30°C and 35°C (Table V.3).

b. Alkaline fading reaction of BG⁺ carbonium ion- The effect of temperature on the alkaline fading reaction of BG⁺ carbonium ion in presence of CTAB was investigated by recording the values of first order rate constant at fixed concentrations of surfactant (0.02 M) substrate (1.8×10^{-5} M) and the reactant (0.0001 M) at temperatures 15°C, 20°C, 25°C and 30°C (Table V.3).

c. Alkaline fading reaction of MG⁺ carbonium ion- The effect of temperature on the alkaline fading reaction of MG⁺ carbonium ion in presence of CTAB was studied by finding the first order rate constant at temperatures 15°C, 20°C, 25°C and 30°C at fixed concentrations of detergent (0.02 M) substrate (1.8×10^{-5} M) and the reactant (0.0001 M). The kinetic data are summarized in Table V.3.

d. General features of the effect of temperature on the reaction of triphenylmethyl carbonium ions with hydroxyl ion in presence of CTAB- It has been observed that the plot of log k vs 1/T for these reactions in presence of CTAB gives straight line which demonstrates the applicability of Arrhenius equation for the evaluation of thermodynamic parameters of these reactions in the micellar environment.

V.5 DISCUSSION

There are several factors which might contribute to the observed influence of organic solvents in altering the overall

micellar effects on the chemical reactions. Bruice and Cordes²⁴ have interpreted the effect of alcohols viz., ethanol, 1-butanol, 1-heptanol and 1-decanol on the reaction of methyl ortho-benzoate in presence of SDS by considering following factors:

(i) replacement of substrate, methyl orthobenzoate, from the micellar phase by alcohol molecules; (ii) changed in the aggregational properties of the detergent and (iii) modification in the electrostatic stabilization of transition state of the reaction. Various factors, for assigning realtive weightage to them, could not be distinguished by these authors.²⁴ Blandamer and Reid²³ in addition to above mentioned factors also considered the destabilization of hydroxyl ions as a contributory factor to explain the micellar effects on the reaction between hydroxyl ion and 2,4-dinitrochlorobenzene in presence of CTAB. It is now proposed that following factors might also be playing an important role in modifying the overall micellar effects on the reaction rates in presence of micelle forming surfactants viz., (i) substantial reorganization in the structure of catalytic micelles as a result of the changes in the aggregational properties of the detergent and the substrate and the participation of solvent molecules in the formation of altogether new aggregates which may have different catalytic efficiency. (ii) Complete destruction of catalytic micelles. (iii) Changes in the thermodynamic parameters of the reaction in presence of surfactant and the solvent. (iv) Change in the activity of water in presence of solvent in micellar environment and (v) Solute-solvent interactions in micellar and the

motion of solvent molecules along with reactants along the reaction coordinates as also in aqueous media.⁹ Under specified reaction conditions some of the considered factors may be eliminated as non-contributory towards overall observed effects.

At low percentage of solvents viz., acetone, dioxane and alcohols except methyl alcohol in the reaction system the reaction of triphenylmethyl carbonium ions viz., SG^+ (see Appendix I), BG^+ and MG^+ with hydroxyl ion is retarded with increasing solvent concentration.^{19,20} However, in the micellar environment of SDS, the increasing concentration of all the nonaqueous solvents in the reaction system decreased the extent of micellar inhibition i.e., increase in the reaction rate is observed (Table V.1). Consequently, these observations clearly eliminates the replacement of substrate from complexed phase to the free bulk phase as the contributory factor towards the observed solvent effects in reducing inhibitory effects of SDS micelles on these reactions. Complete destruction of catalytic micelles in presence of solvents in the reaction system may also be ruled out for the reason that electrostatic as well as hydrophobic interactions will continue to exist in the reaction system. It appears more probable that the complete reorganization in the structure of catalytic micelles would take place. In the formation of new aggregates substrate, detergent, solvent molecules counter ions and/or reactant species would participate. Thus the reorganization of the concentrations of the reactants at reaction site in presence of solvent and the changes in the thermodynamic parameters of the reactions may be

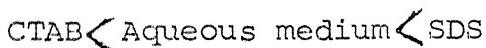
contributory factors towards the solvents effect in diminishing SDS inhibition of these reactions. Breaking of water structure and the consequent destabilization of hydroxyl ions may be another factor contributing towards overall effects in presence of solvents.

Micellar catalysis of triphenylmethyl carbonium ions with hydroxyl ion in presence of CTAB is reduced upon the introduction of ethanol, butanol and acetone in the reaction system (Table V.2, and Figs. V.3 and V.4). These results are in agreement with the finding of other authors.²²⁻²⁴ Ethylene glycol in the beginning enhances the micellar catalysis further and then reduces it with with increasing solvent concentration. These results can also be rationalized by assuming the participation of solvent molecules in reorganizing the structure of catalytic micelles. As a result of this reorganization, the concentrations of reactants at reaction sites would change and the thermodynamic parameters of the reactions would be perturbed.

The effect of ethylene glycol on the above CTAB catalysed reactions could be rationalized as follows: At low concentrations of ethylene glycol, in the absence of CTAB, the rate of reaction of triphenylmethyl carbonium ion is enhanced with increasing solvent concentration (see Appendix I). The pK value of ethylene glycol is high³⁶ and thus the possibility of introduction of a new reaction path³⁶ is excluded to explain such anomalous effects of this solvent. These results are explainable if we consider the destabilization of hydroxyl ions in presence of

solvent and the motion of solvent molecules along with reactants along the reaction coordinates. These effects are possibly further enhanced in presence of CTAB and thus one observes the enhancement in micellar effects of CTAB on these reactions in presence of ethylene glycol. At higher solvent concentration destruction of catalytic micelles^{20,21} might be a contributory factor to the observed decrease in micellar effects.

Inspection of the data concerning the activation parameters of these reactions (Table V.4) shows that the activation energy for the reaction of SG⁺ in carbonium ion with hydroxyl ion in the absence of detergents in aqueous medium is 13.13 kcal. In presence of SDS and CTAB separately activation charged to 17.04 and 10.36 kcal respectively. Similarly for BG⁺ and MG⁺ carbonium ions the value of activation energy showed an increase in presence of SDS and a decrease in presence of CTAB. In general, the values of activation energies in aqueous medium in the absence of detergents and in the presence of CTAB and SDS could be arranged in the following order:



The entropy of activation in presence of CTAB, SDS and also in absence of detergents for these reactions is negative. This demonstrates that the reactions are ionic in character in aqueous as well as in the micellar environments.¹⁸⁻²⁰ Further, it may be observed that the magnitudes of negative activation entropy is in the order;



Table V.4. The values of thermodynamic quantities of activation for the reaction of triphenylmethyl carbonium ions with hydroxyl ion at 25°C.

Sl. No.	Activation parameter	The Reaction of hydroxyl ion with		
		SG ⁺ ion	BG ⁺ ion	MG ⁺ ion
<u>In Presence of 0.02 M CTAB</u>				
1.	ΔE^\neq (kcal mol ⁻¹)	10.36	9.05	11.04
2.	Z_1 (l.mol ⁻¹ sec ⁻¹)	3.53×10^7	3.44×10^9	1.10×10^8
3.	ΔS^\neq (kcal K ⁻¹ mol ⁻¹)	-25.70	-21.76	23.89
4.	ΔH^\neq (kcal mol ⁻¹)	24.08	11.51	9.41
5.	ΔF^\neq (kcal K ⁻¹ mol ⁻¹)	17.42	20.24	16.53
<u>In Absence of Surfactant</u>				
1.	ΔE^\neq (kcal mol ⁻¹)	13.13	12.33	14.40
2.	Z_1 (l.mol ⁻¹ sec ⁻¹)	2.42×10^8	6.63×10^8	6.07×10^{10}
3.	ΔS^\neq (kcal K ⁻¹ mol ⁻¹)	-21.86	-20.26	-11.27
4.	ΔH^\neq (kcal mol ⁻¹)	20.21	11.93	13.80
5.	ΔF^\neq (kcal K ⁻¹ mol ⁻¹)	13.70	18.27	17.16
<u>In Presence of 0.005 M SDS</u>				
1.	ΔE^\neq (kcal mol ⁻¹)	17.04	16.35	18.15
2.	Z_1 (l.mol ⁻¹ sec ⁻¹)	2.24×10^9	3.57×10^9	5.70×10^{11}
3.	ΔS^\neq (kcal K ⁻¹ mol ⁻¹)	-17.86	-15.09	-6.79
4.	ΔH^\neq (kcal mol ⁻¹)	27.09	10.45	17.56
5.	ΔF^\neq (kcal K ⁻¹ mol ⁻¹)	21.77	14.94	19.58

This shows that charge difference between reactants in presence of CTAB is highest and that in SDS is lowest, or in other words association of triphenylmethyl carbonium ions in CTAB, in some way, increases the overall positive charge whereas SDS reduces this charge upon complexation.

However, it should be pointed out that the determination of ΔS^\neq and ΔF^\neq in micellar environment requires the values of bimolecular rate constant in the same media; which in turn requires the exact hydroxyl ion concentration around catalytic micelles. Thus the values of ΔF^\neq and ΔS^\neq which have been calculated are either upper or lower limits of these quantities. In presence of SDS the overall hydroxyl ion concentration will be smaller than that reacting around catalytic aggregates thus the value of bimolecular rate constant would be larger than that used. Thus ΔS^\neq and Z so calculated are the lower limits of this quantities in presence of SDS. Similarly in presence of CTAB the values reported for these quantities correspond to upper limits of these parameters. The values of ΔF^\neq in SDS and in CTAB correspond to upper and lower limits, respectively.

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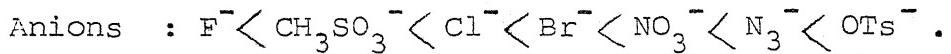
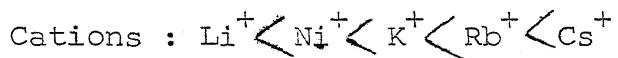
CHAPTER VI

ANALYSIS OF DATA CONCERNING MICELLAR
EFFECTS ON CHEMICAL REACTIONS AVAILABLE
IN THE LITERATURE

VI.1 ABSTRACT

The equations and methods developed in Chapter II have been applied for the analysis of data, concerning micellar influence on reactions, available in the literature. It is concluded that

(i) the substrate plays a significant role in determining the nature and composition of catalytic aggregates which are formed in the reaction system; (ii) the addition of counter ions to the reaction system does not necessarily results in the replacement of the substrate from complexed phase to that of aqueous bulk phase; (iii) alteration in the reactant concentration in the vicinity of catalytic micelles and change in thermodynamic parameters of the reaction are the factors responsible for observed micellar i.e., detergent and also counter ion, effects; (iv) the value of the degree of counter ion ionization of the catalytic aggregates in presence of various counter ions may not be same and this difference is probably responsible for the relative difference in their effectiveness to different extent, (v) the relative values of the factor $f \cdot K_e$ as postulated in Chapter II could be taken as the measure of the effectiveness of counter ions in altering overall micellar influence on chemical reactions and (vi) the counter ion in the order of their effectiveness may be arranged as follows:



VI.2 INTRODUCTION

The optimism that the reaction catalysed by micelle-forming surfactants could serve as valuable analogues for the study of microenvironmental factors which affect the high efficiency of chemical transformations in the biological realm and subsequent efforts to develop such biochemical model systems witnessed careful accumulation of experimental data concerning micellar effects on a large variety of chemical reactions.¹⁻⁶ Several attempts which have been made so far for the quantitative analysis and interpretation of kinetic data for micellar effects on chemical reactions presume that the micellar properties of the surfactants remain unaltered in presence of substrate, reactant, and electrolytes/buffers in the reaction system.⁷⁻¹³ Investigations have also been carried out to determine the fundamental micellar properties such as size, shape, stability, counter ion binding, substrate location, and micropolarity in the stern layer and micellar core in order to supplement the necessary data required by these theories.¹⁴⁻¹⁹ However, an experience reveals that the nature and the extent of overall micellar influence on the reactions, at least in part, depends upon the intrinsic characteristics viz., charge and hydrophobicity of substrate molecules.¹⁻⁶ This points out towards an active participation of substrate and other species in determining the nature and composition of catalytic micelles which are formed in the reaction system.

One of the primary objectives of the present studies is to identify and understand the characteristic features of micella-

influence on the chemical reactions. In Chapters II and IV the model schemes, based upon the mutual interactions of various species present in the reaction system, have been proposed and formulated for the quantitative understanding of micellar effects on chemical reactions. Subsequently, in Chapter IV, the derived equations have been used to analyze micellar effects on the reaction of triphenylmethyl carbonium ions with hydroxyl ion.

The equations have been further used to analyze the micellar data of chemical reactions available in the literature and to resolve discrepancies, if any, in the mechanistic interpretation of the concerned effects. This has been done to check the applicability of the models (Chapter II) in a wider prospect and to draw conclusions, which are generalized in scope and unified in their contents, about the micellar influence on chemical reactions.

VI.3 METHODS

VI.3.1 Procurement of Experimental Data

The data available in tabular and graphical form were collected for the purpose of analysis of micellar influence on chemical reactions for the effect of concentrations of detergent and counter ions. The data from the graphs were obtained after sufficient magnification of the figures by photographic reproduction.

VI.3.2 Analysis of Micellar Data

Analysis of kinetic data for chemical reactions in presence of micelle-forming surfactants was done on the basis of model

schemes presented in Chapter II following the procedure described therein.

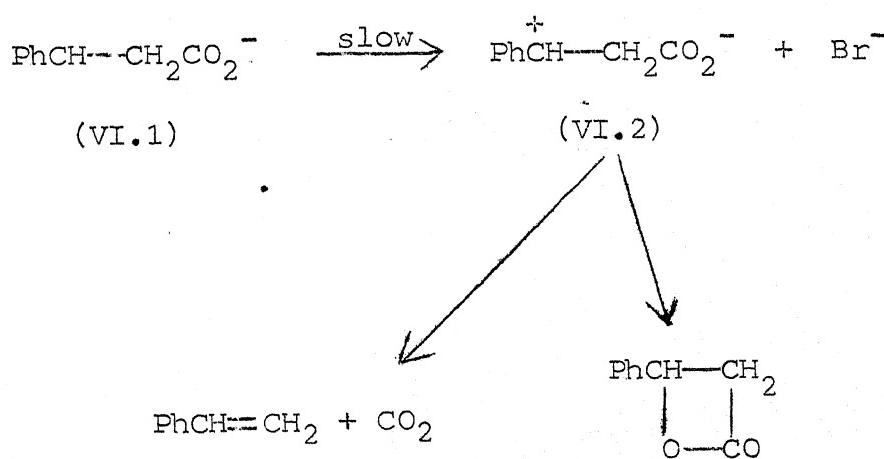
VI.4 ANALYSIS AND INTERPRETATION OF MICELLAR DATA

VI.4.1 REACTIONS CONFORMING TO SCHEME II.1

Systematic studies of the micellar influence on chemical reactions conforming to Scheme II.1 are scarce. The kinetic data of the reactions; viz., decarboxylation of 3-bromo-3-phenylpropionate²¹ ion and the reaction of crystal violet carbonium ion with cyanide ion²² for the effect of concentrations of surfactant and counter ions were accessible to the author. The micellar data for these reactions has been analyzed and interpreted on the basis of Scheme II.1.

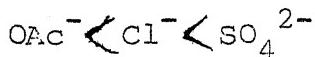
a. Micellar data for decarboxylation of 3-bromo-3-phenylpropionate:

Bordwell and Knipe²⁰ have established that the decarboxylation of 3-bromo-3-phenylpropionate ion (VI.1) involves ionization to give a carbonium ion (VI.2) as the rate determining step. This carbonium ion either decarboxylates or cyclizes to a lactone.



Bunton et al.²¹ have reported that rate of this decarboxylation reaction is inhibited in presence of cationic micelle-forming surfactant cetyltrimethylammonium bromide (CTAB). The counter ions with increasing concentration were found to decrease the extent of overall inhibition caused by CTAB. These authors assigned the effect of inhibition to the stabilization of the species (VI.1) by CTAB. The influence of counter ions was rationalized in terms of the displacement of the substrate (VI.1) by the anions from the complexed micellar phase to the aqueous bulk phase.

Analysis of micellar data (see, Figs. VI.1 and VI.2) on the basis of Scheme (II.1) gives the value of n , the cooperativity index corresponding to detergent CTAB, equal to 4.16. The values of p , cooperativity index corresponding to anions, and that of binding constant, K_{b1} , in presence of various counter ions (see, Table VI.1) vary in the order:



It is obvious that in the process of interaction between substrate and the detergent, the initial state is stabilized (VI.1) due to relative localization of negative charge on this species by the oppositely charged surfactant species. Consequently, the formation of carbonium ion (VI.2) is retarded. The increase in the value of overall binding constant K_{b1} , as postulated in Scheme II.1 may be rationalized in terms of the incorporation of counter ions in the catalytic aggregates. Large size and low charge density anions are more effective in this respect.

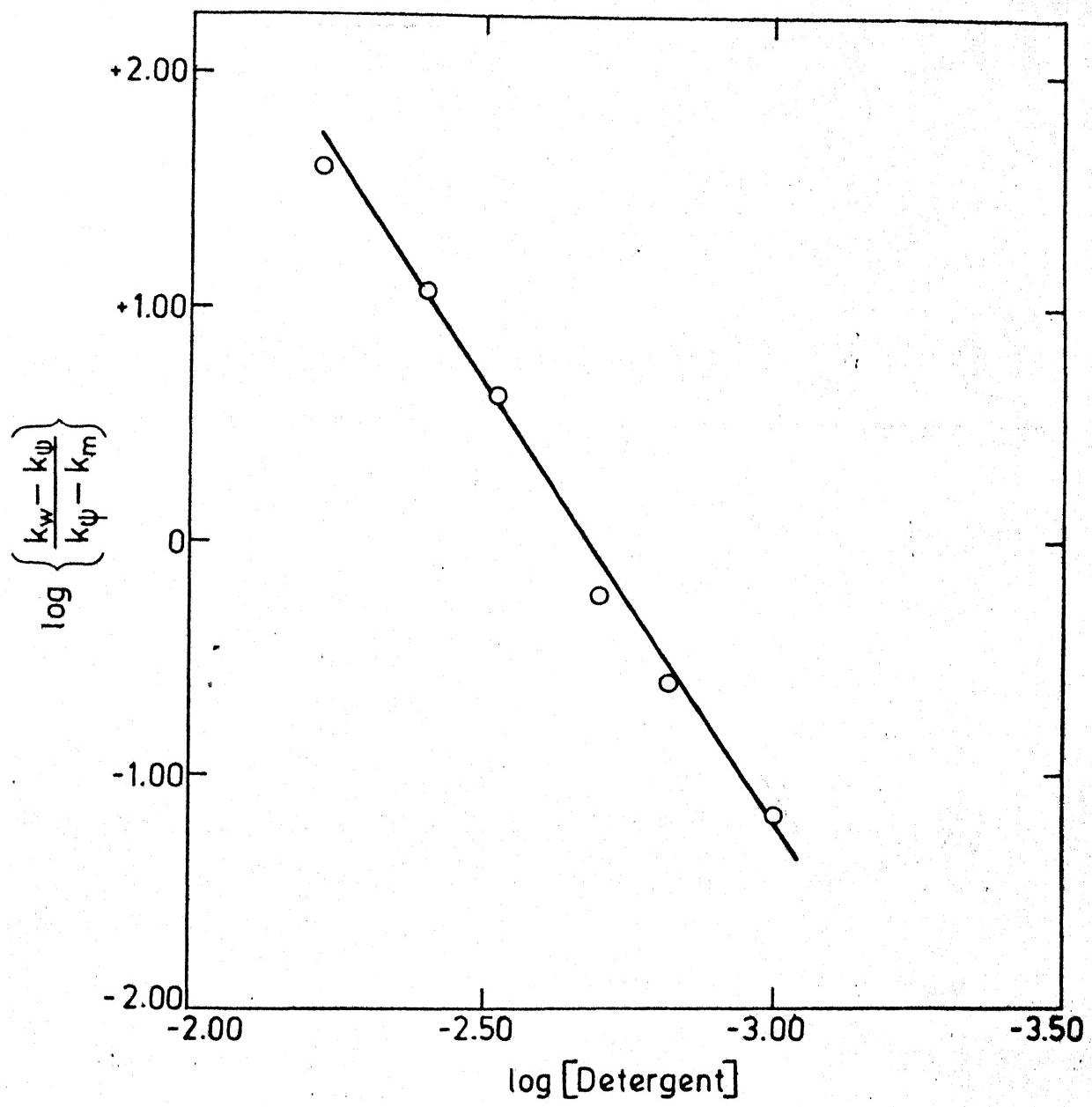


Fig.VI.1 Analysis of the effect of CTAB concentration on the decarboxylation reaction of 3-bromo-3-phenyl-propionate at 25°C.

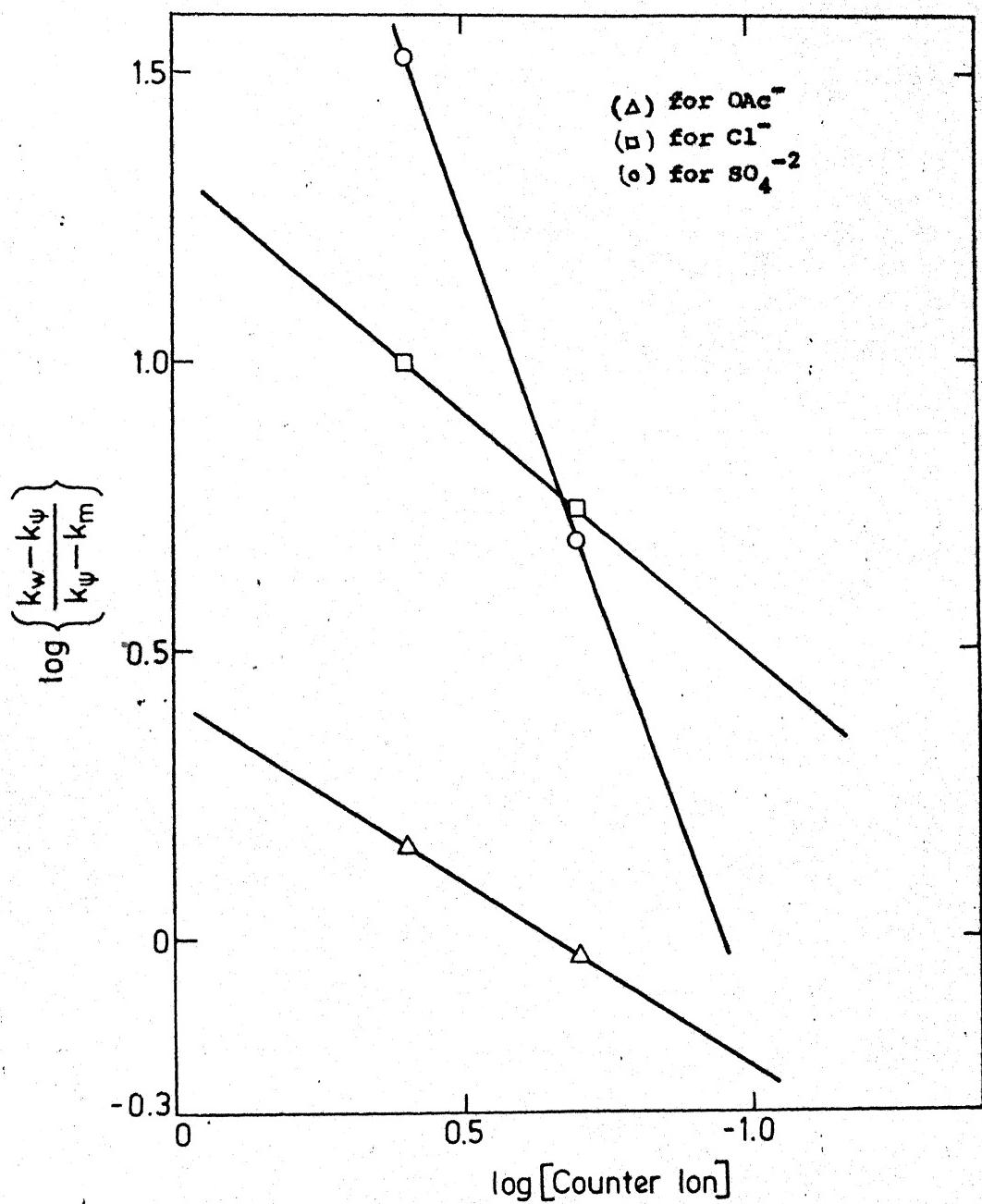


Fig.VI.2 Quantitative treatment of kinetic data for the effect of anions on decarboxylation reaction of 3-bromo-3-phenyl-propionate in presence of CTAB on the basis of scheme II.1

Table VI.1. Analysis of micellar data for decarboxylation reaction of 3-bromo-3-phenylpropionate in presence of CTAB at 25°C.

(Data collected from ref. 21)

L. D.	Counter Ion	No. (s) Analogous to Cooperativity Index		Binding Constant, K_{b1}
		n, corres- ponding to detergent	p, corres- ponding to counter-ion	
1.	OAc ⁻		0.64	5.46 x 10 ⁸
2.	Cl ⁻	4.16	0.82	4.35 x 10 ⁹
3.	SO ₄ ⁻²		1.13	2.00 x 10 ¹⁰

Table VI.2. Quantitative analysis of counter ion effects on SDS inhibited reaction of crystal violet carbonium ion with cyanide ion at 25°C.

(Data collected from ref. 22)

L. D.	Counter Ion	No. (s) Analogous to Cooperativity Index		Binding Constant, K_{b1}
		n for SDS	p for Cations	
.	Na ⁺		2.24	2.71 x 10 ¹¹
.	K ⁺		2.57	5.40 x 10 ¹¹
.	NH ₄ ⁺	5.05	2.66	5.82 x 10 ¹¹
.	Cd ⁺²		4.35	4.70 x 10 ¹³
.	Zn ⁺²		4.37	5.64 x 10 ¹³

Since the studies concerning the effect of counter ion on the overall inhibition caused by the presence of CTAB were conducted at detergent concentration much higher than the saturation concentration in rate vs surfactant concentration profile,²¹ the replacement of hydrophobic substrate by small hydrophilic ions seems improbable. The effect of counter ion, however, may be explained as follows:

The incorporation of counter ions in the catalytic aggregates should result in the neutralization of charges on CTAB head groups. As the charges on the catalytic micelles are neutralized the species (VI.1) gets destabilized compared to the situation when no counter ions were present in the reaction system. This facilitates the conversion of substrate (VI.1) to the carbonium ion (VI.2) but not to the same extent as in the absence of the detergent in the reaction system. Thus, the neutralization of charge on catalytic micelles rather than the displacement of the substrate from complexed phase to aqueous bulk are factors responsible for observed effects of counter ions on micellar inhibition of this reaction as inferred by Bunton et al.²¹

b. Data for sodium dodecyl sulfate inhibited reaction of crystal violet with cyanide ion- The reaction between triphenylmethyl carbonium ion (CV^+), obtained from crystal violet (CV) and cyanide ion in aqueous media, has been reported²² to be inhibited in presence of anionic micelle-forming surfactant sodium dodecyl sulfate (SDS). The extent of inhibition caused by SDS is reduced with

the increasing concentration of counter ions viz., Na^+ , K^+ , NH_4^+ , Cd^{+2} and Zn^{+2} . In the reaction system containing CV^+ , SDS, CN^- and any of the above mentioned counter ions, CN^- ions would be excluded from the formation of catalytic aggregates as this ion bears a charge similar to that of SDS and may be possessing only insignificant hydrophobicity. The competition between counter ions and the reactant ion is not operative in this reaction system and thus it conforms to Scheme II.1.

Analysis of the micellar data on the basis of Equation (2.7) for the effect of detergent concentration on the reaction rate gives the value of n , cooperativity index corresponding to SDS equal to 5.05 (Table VI.2). The effect of SDS on this reaction is explainable in terms of the stabilization of ground state with respect to transition state and the non-accessibility of reactant cyanide ion to the complexed crystal violet carbonium ions.

Analysis for the effect of counter ions (Fig. VI.3) on the overall inhibition caused by SDS on the basis of Equation (2.7) gives the values of p and K_{b1} corresponding to different cation. It may be observed (Table VI.2) that the values of p and the overall binding constant, K_{b1} , in presence of various counter ions increase with increasing size and low charge density of cation in a given series of monovalent or divalent ions. In view of the highly hydrophobic nature of the substrate, CV^+ carbonium ion, and the existence of favourable electrostatic interaction between the detergent and substrate species, the replacement of crystal violet carbonium ions from complexed phase to aqueous

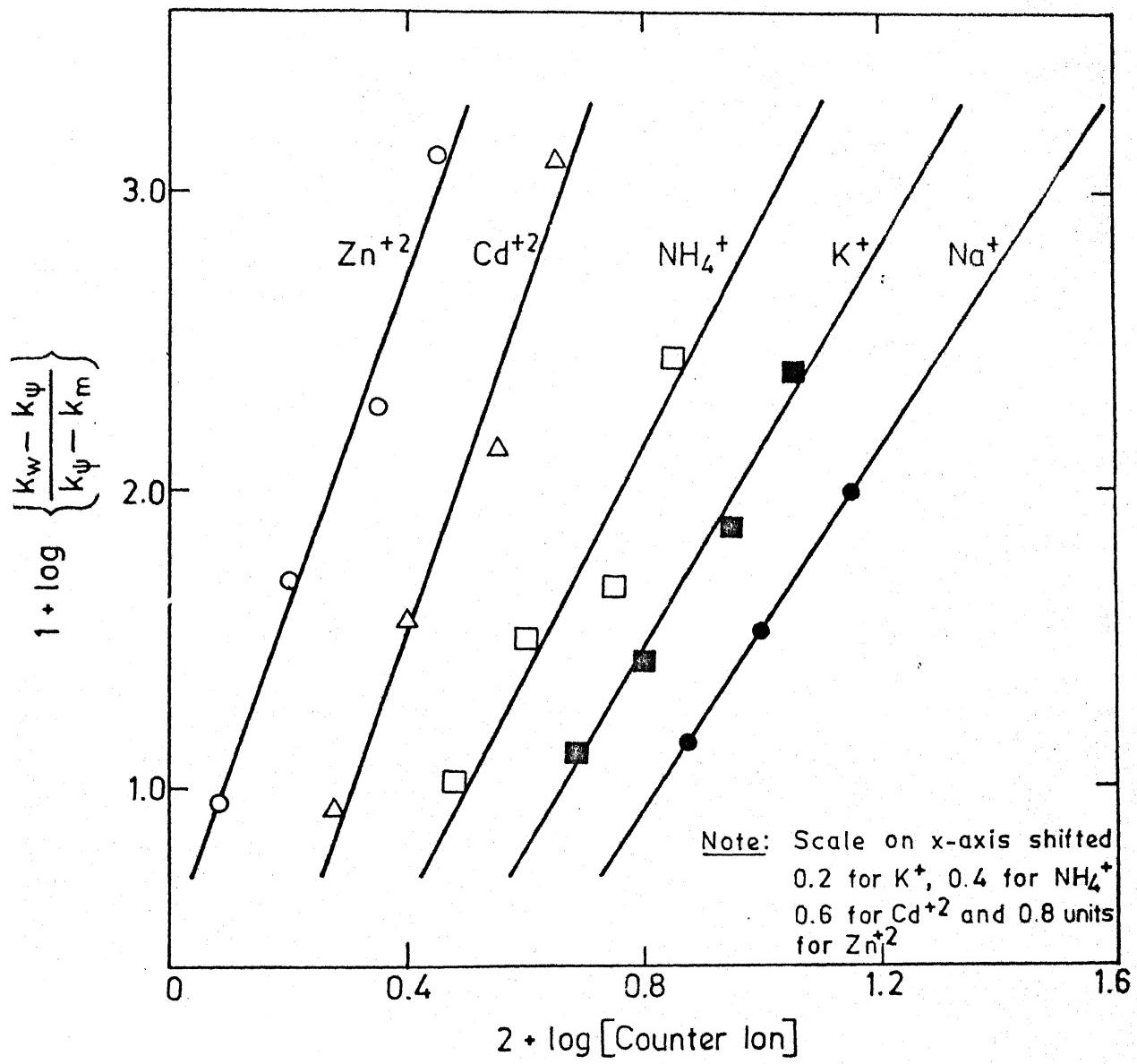
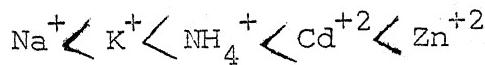


Fig.VI.3 Treatment of the effect of cations on SDS inhibited alkaline fading reaction of crystal violet carbonium ion at 25°C on the basis of scheme II.1.

bulk phase by hydrophilic counter ions seems quite improbable. This is particularly true as the studies of counter ion effects on this reaction were carried out²² at surfactant concentration well above the saturation concentration in rate vs SDS concentration profile. Thus, one may conclude that the incorporation of counter ions in catalytic aggregates result in subsequent neutralization of the charges carried by them. In this process the ground state of the reaction will get relatively destabilized compared to the situation when there were no added counter ions but only those derived from the detergent were present in the reaction system. Further, this neutralization will relatively facilitate the attack of cyanide ion upon the carbonium ions in the complexed phase and therefore overall extent of inhibition caused by SDS would be reduced.

The extent to which counter ions would be able to annul the effect of SDS and consequently increase the reaction rate would depend upon the relative destabilization of the ground state of the reaction and on the facility provided to cyanide ion to attack the carbonium ion. The capability of counter ions to do so is directly related to their incorporation in/on the catalytic micelles which is reflected in the values of p and K_{b1} corresponding to concerned ion. Thus, cations may be arranged in the order of their efficiency to alter micellar effects on the basis of this reaction as;



VI.4.2 REACTIONS CONFORMING TO SCHEME II.2

In the reactions analyzed in the following pages, the reactant also serves as one of the counter ions thus the reactive as well as nonreactive ions in such cases compete for sites in/or the catalytic aggregates. These reactions conform to Scheme II.2.

a. Alkaline fading reaction of crystal violet- Albrizzio *et al.*²⁴ have extended the studies for the effect cationic micelle-forming surfactant cetyltrimethylammonium bromide (CTAB) and further the effect of several ions on the overall catalysis in presence of CTAB on the reaction of crystal violet (CV^+) carbonium ion with hydroxyl ion. The reactant hydroxyl ion serves as the counter ion for CTAB. Therefore in the reaction system containing CV^+ , OH^- , CTAB and counterions, there would be a competition between reactant and the counter ions for sites in/or the catalytic aggregates. The reaction system therefore conforms to Scheme II.1.

Analysis of the effect of detergent concentration for this reaction was done on the basis of this scheme (Fig. VI.4) to obtain the value of n , corresponding to cooperativity index of detergent. The values of various parameters which explain the observed micellar effects are summarized in Table VI.3. The experimental results are compared with the theoretically generated plots (Fig. VI.5) which were obtained in the process of analysis of data for the effect of counter ions on the micellar catalysis of CTAB.

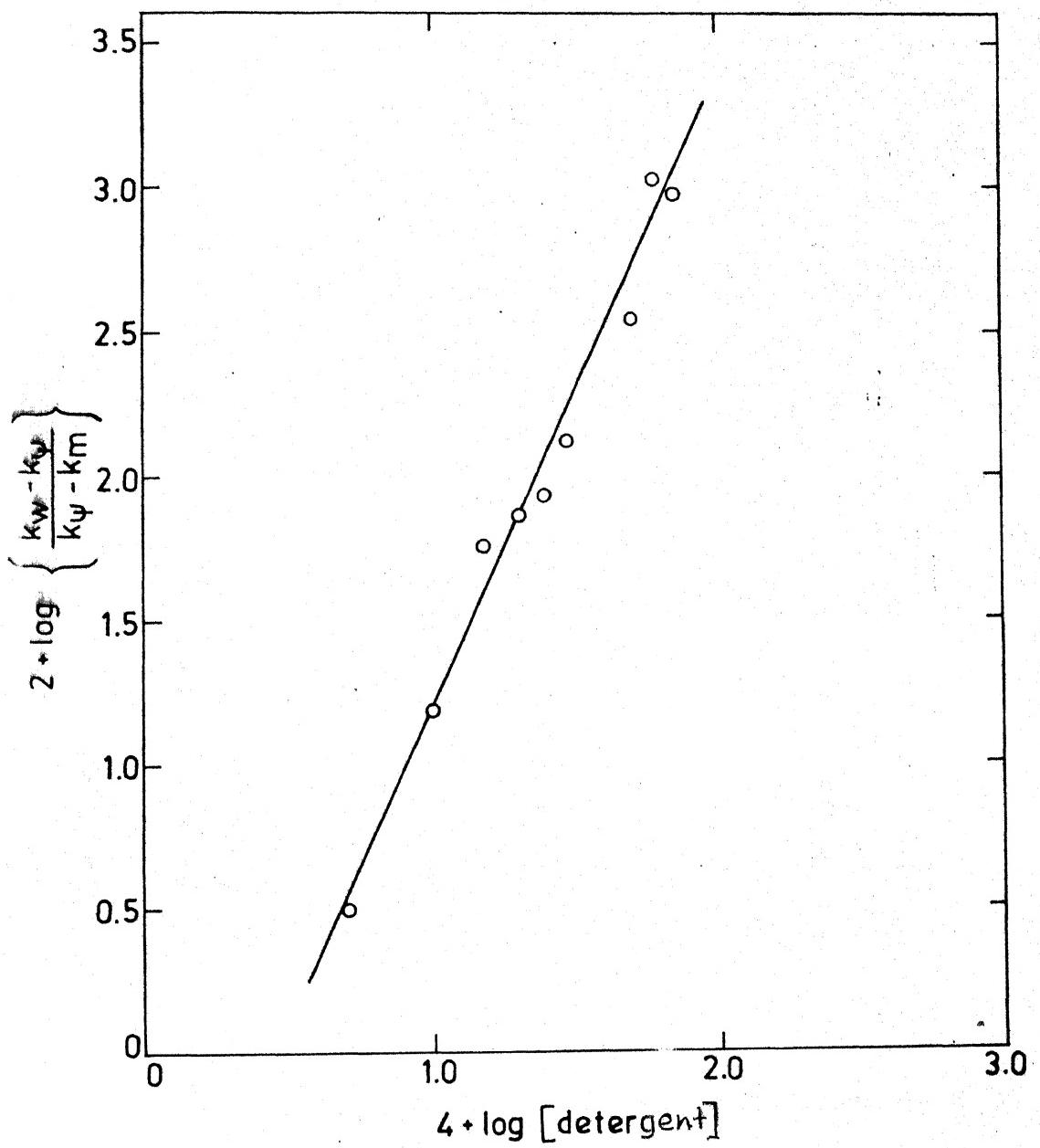


Fig. VI.4 Analysis of the effect of CTAB concentration on the alkaline fading reaction of crystal violet (C.V.) carbonium ion at 30°C

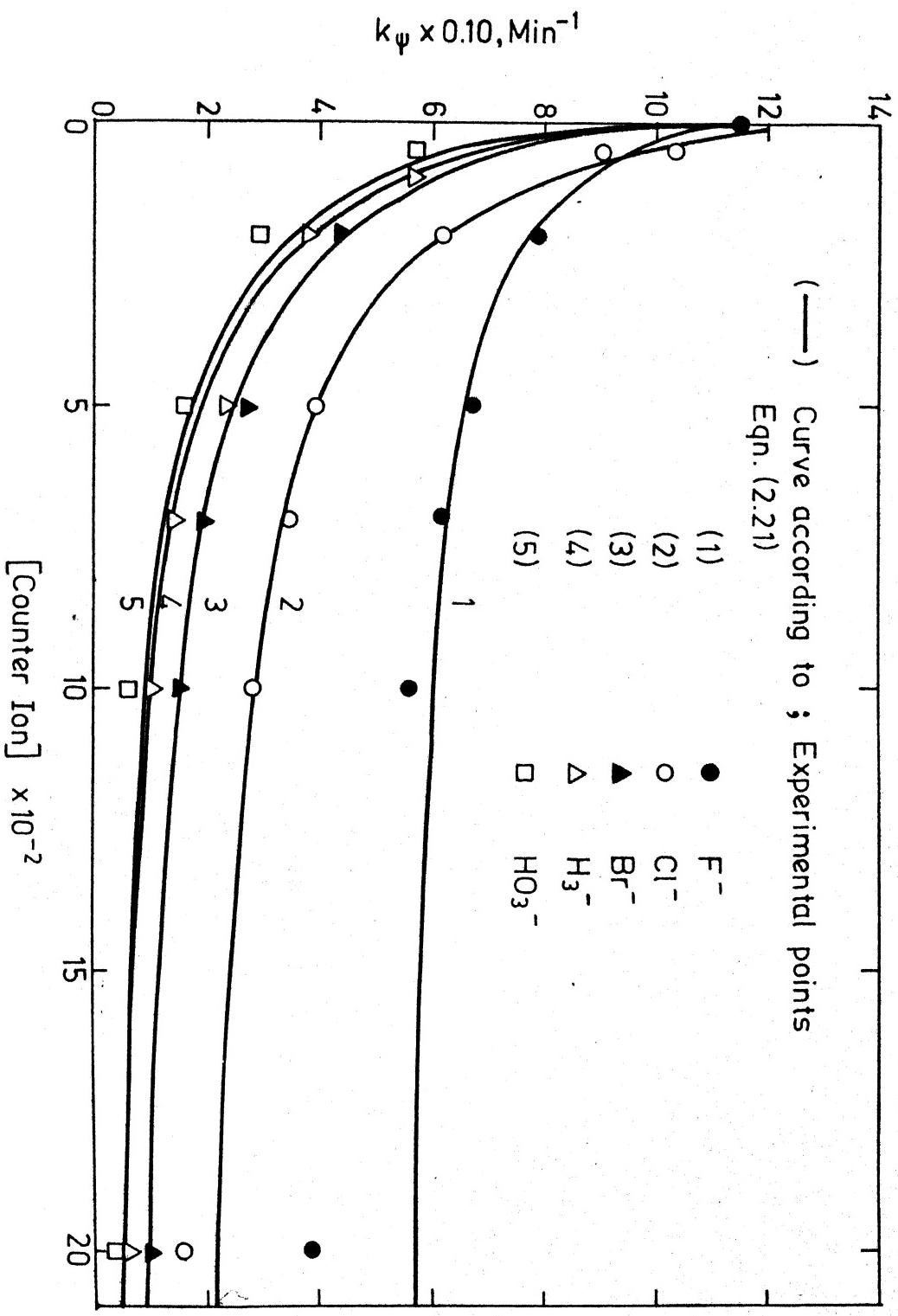


Table VI.3. Analysis of the reaction of crystal violet (CV) carbonium ion with hydroxyl ion in presence of CTAB at 25°C according to Scheme II.2.

Sl. No.	Counter Ion	Nos. (s) Corresponding to <u>Cooperativity Indexes</u>		Factor, $f \cdot K_e$	Binding Constant K_{b2}
		n for CTAB	p for anions		
1.	F ⁻		0.050	1.23×10^6	5.70×10^3
2.	Cl ⁻		0.140	1.09×10^6	2.26×10^5
3.	Br ⁻	2.02	0.320	3.93×10^5	9.10×10^5
4.	N ₃ ⁻		0.600	2.28×10^5	1.21×10^7
5.	NO ₃ ⁻		0.810	1.00×10^5	3.93×10^6

Table VI.4. Quantitative treatment of micellar data for the reaction of 2,4-dinitrofluorobenzene with hydroxyl ion at 25°C in presence of CTAB according to Scheme II.2

Sl. No.	Counter Ion	No. (s) Analogous to <u>Cooperativity Index</u>		Factor, $f \cdot K_e$	Binding Constant, K_{b2}
		n	p		
1.	F ⁻		0.010	7.12×10^6	4.20×10^3
2.	CH ₃ SO ₃ ⁻		0.510	1.67×10^5	3.52×10^4
3.	Cl ⁻	2.87	0.750	4.97×10^4	4.54×10^4
4.	Br ⁻		1.74	4.57×10^4	2.99×10^6
5.	NO ₃ ⁻		2.79	2.25×10^4	1.11×10^8

Table VI.5. Quantitative treatment of the micellar data for the reaction of p-nitrophenyl-hexanoate with a hydroxyl ion in presence of TDTACl at 25°C (Scheme II.2).

Sl. No.	Counter Ion	No. (s) Analogous to <u>Cooperativity Index</u>		Factor, $f \cdot K_e$	Binding Constant, K_{b2}
		n	p		
1.	F ⁻		0.460	1.45×10^4	9.87×10^{10}
2.	Cl ⁻	4.47	0.550	5.66×10^3	4.40×10^{11}
3.	Br ⁻		1.41	1.98×10^3	1.59×10^{12}
4.	NO ₃ ⁻		1.87	1.23×10^3	1.07×10^{14}

b. Reaction of 2,4-dinitrofluorobenzene with hydroxyl ion- The effect of cetyltrimethylammonium bromide on the reaction of 2,4-dinitrofluorobenzene with hydroxyl ion has been reported by Bunton and Robinson.²⁵ The effect of various electrolytes viz., NaF, LiCl, NaCl, KCl, $(\text{CH}_3)_4\text{NCl}$, NaBr, NaNO_3 , $\text{CH}_3\text{SO}_3\text{Na}$ etc. on the micellar catalysis in presence of 0.025 M CTAB was studied. A small contribution of the effect of co-ion in reducing the overall efficiency of CTAB in catalysing this reaction was suspected on the basis of these studies. The effect of electrolytes on this reaction in presence of CTAB was attempted on the basis of Scheme II.1. The theoretically generated curves along with the experimentally obtained points for the effect of counter ions on this reaction in presence of CTAB, are shown in Fig. VI.6. It is proper to mention here that difficulties were encountered while analyzing the effect of chloride ion on the micellar catalysis. As mentioned earlier the effect of chloride ions obtained from several electrolytes viz., LiCl, KCl, NaCl and $(\text{CH}_3)_4\text{NCl}$ was studied in this reaction system and the influence of cations on such an effect was inferred. In the first instance the effects of chloride ions obtained from various electrolytes was analyzed separately which resulted in large errors when the theoretically generated curves were matched with the results obtained experimentally. In the second instance the arithmetic average value of rate constant, k_ψ , was evaluated at different chloride ion concentrations. The values of k_ψ at different chloride ion concentration were used to analyze the effect of this ion on

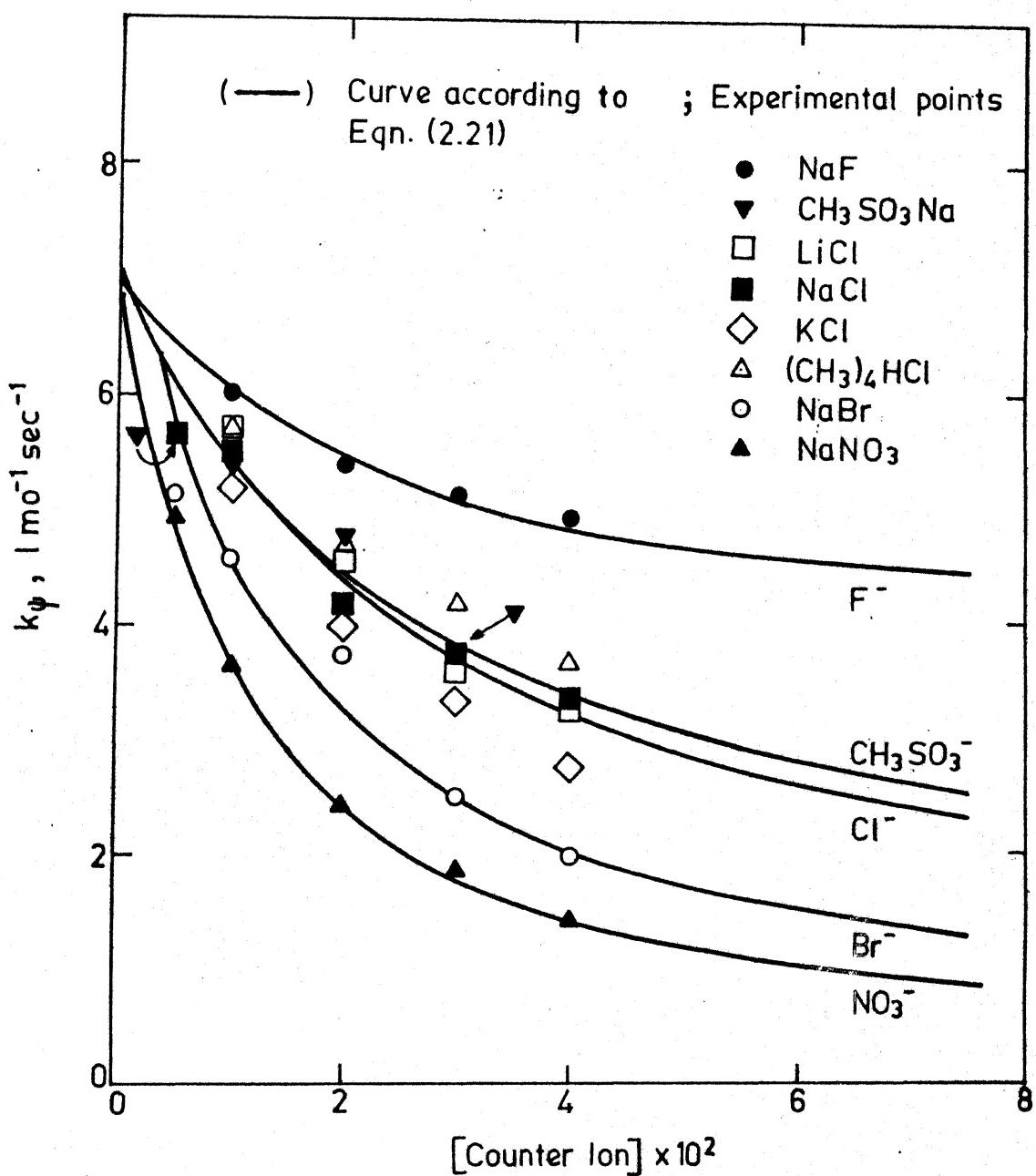


Fig.VI.6 Quantitative analysis of the effect of counter ions on the reaction of 2,4-dinitrofluorobenzene with hydroxyl ion in presence of 0.025M CTAB at 25°C.

micellar catalysis. Surprisingly, an error of the order of $\pm 5\%$ was recorded (Fig. VI.6) between theoretically calculated and the experimentally obtained k_{ψ} values (average) for various counter ion concentration. This very clearly demonstrated that the co-ions do not play any significant role in altering the efficiency of micellar effects. The values of various parameters n , p , $f \cdot K_e$ and K_{b2} for the micellar influence of CTAB on this reaction are summarized in Table VI.4.

c. Hydrolysis of p-nitrophenyl hexanoate in presence of tetradecyltrimethylammonium chloride- Romsted and Cordes have studied the hydroxide ion dependent hydrolysis of p-nitrophenyl hexanoate in presence of alkyl trimethylammonium detergent salts. The effect of concentration of tetradecyltrimethylammonium chloride (TDTACl) on the reaction rate was examined. The studies were extended to investigate the effect of counter ions viz., F^- , Cl^- , Br^- , NO_3^- and SO_4^{2-} on this reaction at a concentration of TDTACl which was much higher than the saturation concentration in rate vs detergent (TDTACl) concentration profile for this reaction. The comparison of experimental and the theoretically determined rate constants at various counter ion concentrations is shown in Figure VI.7. The values of parameters viz., n , p , $f \cdot K_e$ and K_{b2} corresponding detergent and various counter ion evaluated for this reaction system are summarized in Table VI.5.

d. Reaction of p-nitrophenyl diphenylphosphate with hydroxyl ion in presence of cationic micelle-forming detergent- Bunton and

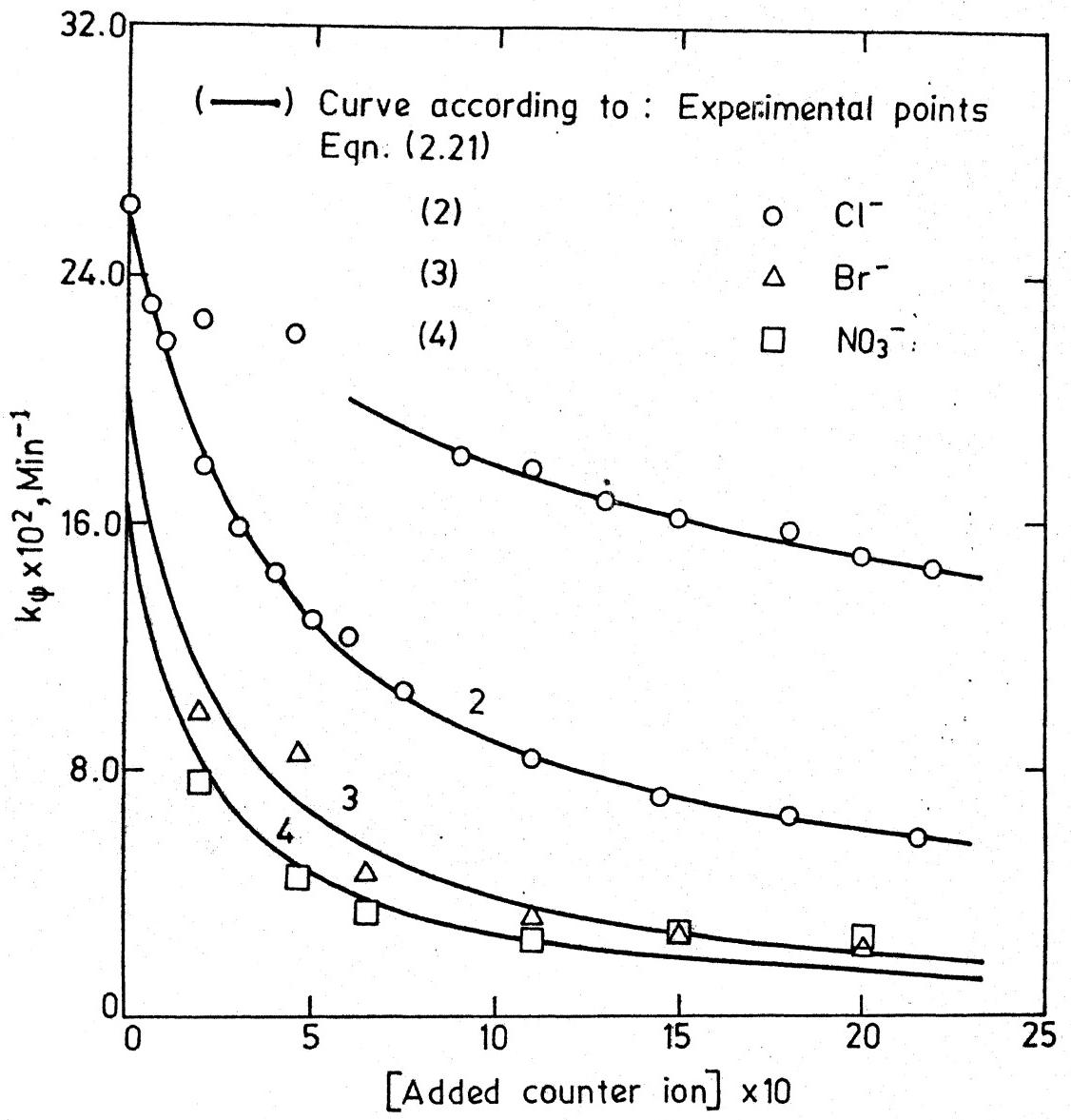


Fig. VI.7 Analysis of the effect of anions on micellar catalysis of the hydrolysis reaction of p-nitrophenyl hexanoate in presence of 0.009M TDTACl at pH 10.15 and 25°C.

coworkers²⁷ have examined the effect of three cationic micelle-forming quaternary ammonium salt viz., phenyl-cetyltrimethylammonium bromide (CPDA), 2,4-dimethoxyphenyl-cetyltrimethylammonium bromide (CDPDA) and 2,4-dimethoxybenzyl-cetyltrimethylammonium bromide (CDBDA) on the reaction of p-nitrophenyl-diphenylphosphate with hydroxyl ion. In these reaction systems catalysis not only begins but also attains saturation well below the critical micelle concentrations of pure surfactants. This demonstrates the participation and role of the substrate in the formation of catalytic aggregates. The studies were extended to examine the effect of counter ions viz., Cl^- , Br^- , CH_3SO_3^- , NO_3^- and OTs^- . The analysis of the effect of detergents concentration and of the effect of several counter ion concentration on micellar catalysis was done following the Scheme II.2. The comparison of experimental data with the numerically calculated curves for the effect of counter ions exhibited a maximum error of ± 15.0 per cent in presence of the detergents CPDA, CDPA and CDBDA respectively. The parameters determined on the basis of this analysis are summarized in Table VI.6.

e. Acid hydrolysis of methyl ortho-benzoate- Dunlop and Cordes²³ have systematically investigated the micellar effects on the reaction of methyl ortho-benzoate carbonium ion with hydrogen ion. The effect of concentration of sodium dodecyl sulfate (SDS) and the effect of cations on the overall catalysis caused by SDS was analyzed on the basis of Scheme II.2. The comparison of

Table VI.6. Analysis of the effect of anions on the micellar catalysis of cationic micelle-forming surfactants on the reaction of p-nitrophenyl diphenylphosphate with hydroxyl ion at 25°C according to Scheme II.2

Reaction	Deter-	Counter	No. (s) Analogous to Cooperativity Index		Factor, $f \cdot K_e$	Binding constant, K_{b2}
			Ion	in Enzymatic reactions		
PNDP + OH ⁻	Deter- gent	Counter Ion	CH ₃ SO ₃ ⁻	1.01	2.52x10 ⁵	1.75 x 10 ⁸
			Cl ⁻	1.01	2.09x10 ⁵	2.11 x 10 ⁸
			Br ⁻	2.10	3.47x10 ³	9.07 x 10 ¹⁰
			NO ₃ ⁻	1.62	1.38x10 ³	2.95 x 10 ¹²
			OTs ⁻	0.60	5.01x10 ²	4.53 x 10 ¹¹
PNDP + OH ⁻	Deter- gent	Counter Ion	CH ₃ SO ₃ ⁻	1.01	2.63x10 ⁵	3.09 x 10 ¹¹
			Cl	1.01	2.49x10 ⁵	3.27 x 10 ¹¹
			Br ⁻	3.02	4.48x10 ³	1.44 x 10 ¹⁴
			NO ₃ ⁻	1.30	2.82x10 ³	2.44 x 10 ¹⁴
			OTs ⁻	0.470	6.72x10 ²	1.92 x 10 ¹³
PNDP + OH ⁻	Deter- gent	Counter Ion	CH ₃ SO ₃ ⁻	1.01	2.33x10 ⁵	4.93x10 ⁶
			Cl	1.01	1.24x10 ⁵	9.46x10 ⁶
			Br ⁻	2.89	2.62x10 ⁴	4.52x10 ⁷
			NO ₃ ⁻	1.15	2.40x10 ³	1.40x10 ⁹
			OTs ⁻	1.01	8.58x10 ²	1.46x10 ⁹

Table VI.7. Analysis of the effect of cations on the micellar catalysis of SDS on the reaction of methyl ortho-benzoate with hydrogen ion according to Scheme II.2

Sl. No.	Cation Concen- tration, M	The value of rate constant, k_{ψ} , $\text{l.mol}^{-1}\text{sec}^{-1}$		R.M.S. Error %
		Experimental	Calculated	
1	2	3	4	5
Cation: Li^+ ; p, Cooperativity Index: 1.01; Temperature: 25°C				
1.	0.01	213000	212604	
2.	0.04	132000	131478	
3.	0.07	95400	93023	1.97
4.	0.10	70800	73063	
5.	0.13	60700	60685	
6.	0.19	45000	45942	
7.	0.25	38200	37339	
<hr/>				
Cation: Na^+ ; (from NaClO_4) p, Cooperativity Index: 1.01; Temperature: 25°C				
1.	0.01	206000	216969	
2.	0.04	108000	109459	
3.	0.07	83000	75161	5.09
4.	0.13	45000	47940	
5.	0.19	35000	37918	
6.	0.25	29400	29005	
<hr/>				
Cation: Na^+ ; (from NaCl) p, Cooperativity Index: 1.07; Temperature: 25°C				
1.	0.01	213000	203856	
2.	0.03	127000	129083	
3.	0.04	111000	108735	2.84
4.	0.05	90000	94368	
5.	0.07	74300	75332	
6.	0.10	59000	58593	
7.	0.13	49400	48378	

..contd.

Table Vi.7 (contd.)

1	2	3	4	5
Cation: K^+ ; p, Cooperativity Index: 1.01; Temperature: 40°C				
1.	0.01	425000	424068	
2.	0.011	412000	410213	
3.	0.015	354000	359640	1.20
4.	0.020	316000	310525	
5.	0.025	272000	273670	
<hr/>				
Cation: Rb^+ ; p, Cooperativity Index : 1.01 : Temperature: 40°C				
1.	0.011	451000	464044	
2.	0.015	396000	371386	
3.	0.020	318000	300101	4.80
4.	0.025	236000	253425	
5.	0.040	168000	175898	
6.	0.070	112000	112363	
7.	0.13	69000	67520	
<hr/>				
Cation: Cs^+ ; p, Cooperativity Index : 1.01; Temperature: 25°C				
1.	0.01	213000	191012	
2.	0.04	84000	86504	
3.	0.07	56000	58282	6.03
4.	0.10	40800	44729	
5.	0.13	36800	36625	
6.	0.19	28100	27247	
7.	0.25	22900	21906	
<hr/>				
Cation : Cs^+ ; p, Cooperativity Index : 1.01 ; Temperature : 25°C				
1.	0.06	21300	21206	
2.	0.09	16200	16521	1.75
3.	0.12	13900	14102	
4.	0.18	11900	11639	

Table VI.8. Reaction parameters for micellar effect on the reaction of methyl ortho-benzoate in presence of SDS according to Scheme II.2

Sl. No.	Counter Ion n	No. (s) Analogous to Cooperativity Index in Enzymatic reactions p	Factor, $f \cdot K_e$	Binding Constant, K_{b2}
1.	Li^+ (25°C)	1.01	1.68×10^6	1.62×10^8
2.	Na^+ (25°C)	1.07	1.81×10^5	1.63×10^9
3.	NH_4^+ (25°C)	1.01	8.36×10^4	3.27×10^9
4.	K^+ (40°C)	1.01	5.08×10^5	—
5.	Rb^+ (40°C)	1.01	2.73×10^5	—
6.	Cs^+ (25°C)	1.02	1.62×10^4	5.47×10^9

numerically generated plots on the basis of Equation (2.21) with experimentally obtained results is shown in Table VI. 7. The values of n , p , $f \cdot K_e$, K_{b2} are summarized in Table VI. 8.

f. General features of reaction conforming to Scheme II.2- On the basis of analysis of reactions, reported in this thesis, which conform to Scheme II.2, following general observations could be made:

(1) The value of n , corresponding to average number of detergent species, which associate with one substrate molecule, depends upon the nature of the substrate as well as that of detergent under consideration.

(2) The values of p , which correspond to average number of counter ions which associate with a catalytic micelle per substrate molecule is dependent upon the nature of counter ion, substrate and detergent present in the reaction system.

(3) The value of $f \cdot K_e$, exchange factor between counter ion and reactant decreases with increasing size and decreasing charge density of the counter ions in all the cases. However, the absolute value of $f \cdot K_e$ in several reaction systems for the same ions are different.

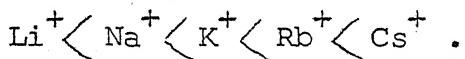
(4) The value of the overall binding constant K_{b2} as postulated in Scheme II.2 in a given reaction system increases with the increasing size and low charge density of counter ions.

VI.5 DISCUSSION

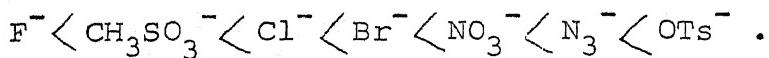
The findings ~~that~~ (i) the value of n in different reaction system is different and (ii) the values of p for various counter ions even in the same reaction system are different, ~~are~~ true for reactions conforming to Scheme II.1 as well as Scheme II.2, which shows that the composition of catalytic micelles to a large extent is determined by the nature of substrate. Further, the degree of counter ion binding also depends upon the nature of counter ion as well as the nature of the catalytic aggregates.²⁸

In any reaction system conforming to Scheme II.1 the value of p , cooperativity index corresponding to counter ion and also that of overall binding constant, K_{b1} , increases with increasing size and low charge density of the counter ions. In all the reaction systems analyzed (Scheme II.2) it was found that the value of $f \cdot K_e$ decreases with increasing size and low charge density of the counter ions. The decrease in the value of $f \cdot K_e$ according to Scheme II.2 means the decrease in the reactant concentration in the vicinity of catalytic micelles. Thus, the counter ion with large size and low charge density are more effective in altering the efficiency of micellar influence of the chemical reactions. This also shows that the effect of inert competing ions on micellar effects is explainable in terms of the replacement of reactive counter ion from the vicinity of catalytic aggregates by these inert ions. The replacement of reactant ions by the inert counter ions to a large extent is determined by the intrinsic characteristics of the concerned ions. This explains why the relative order

of effectiveness of various counter ions is largely independent of the chemical reaction under consideration as pointed out by other workers.^{6,7} Thus the order of decreasing values of $f \cdot K_e$ (Table VI.8), reflects the increasing effectiveness of cations as follows:



Similarly an inspection of Tables VI.3 to VI.6 permits the arrangement of anions in the order of increasing effectiveness as shown below:



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A P P E N D I X

KINETIC STUDIES ON THE REACTION OF CARBONIUM IONS WITH NUCLEOPHILES : ALKALINE FADING OF SETOGLAUCINE

Triphenylmethane dyes are known to provide stable carbonium ion system in aqueous media.¹⁻⁵ Recently, the effect of micelle-forming surfactants on the reaction of carbonium ions with nucleophiles, using these dyes have been reported.⁶⁻¹⁰ Vekhande and Munshi have found that the efficiency of analytical determinations in which these dyes are utilized as reagents, could be enhanced in micellar environment.¹¹⁻¹⁴

Setoglaucine (C.I. Basic Blue 1), abbreviated as SG and chemically known as ($[\alpha - [\alpha - (\text{o-chlorophenyl}) - \text{p-(dimethylamino)} - \text{benzylidene}] - 2,5\text{-cyclohexadien-1-ylidene}]$ dimethylammonium chloride) is one of the members of triphenylmethane dyes series which has industrial and physico-chemical applications.^{15,16} It can be used for quantitative determination of nitrophenols and numerous transition metal ions and as an indicator in cerimetry, iodometry and titrimetry using potassium dichromate. Micellar effects on the reaction of carbonium ion, generated from SG, with hydroxyl ion have recently been reported by the authors,⁹ however, the systematic data concerning the kinetics of this reaction in aqueous media are nonexistent.

In this study the effect of various parameters viz., concentrations of substrate (SG) and reactant (OH^-), ionic strength, temperature and dielectric constant on the alkaline fading reaction

of setoglaucine is reported. The effect of ionic strength and dielectric constant on the thermodynamic quantities of activation of this reaction has also been investigated.

EXPERIMENTAL SECTION

Setoglaucine was obtained from K and K laboratories, Inc., U.S.A. as rare and fine chemical, sodium hydroxide was E. Merck's guaranteed reagent and potassium nitrate, acetone, dioxane, ethylene glycol and other chemicals were B.D.H. AnalaR grade products. Solvents were purified prior to use following usual procedures. Other chemicals were used as obtained. The procedure followed and the equipment used are described earlier.^{5,9}

RESULTS AND DISCUSSION

In aqueous media SG exhibits an intense absorption band at 635 nm. Absorption maxima for this dye in 0.8 M aqueous KNC_3 solution, 20% (v/v) ethylene glycol-water, 40% (v/v) acetone-water and 40% (v/v) dioxane-water mixtures corresponded to 635 nm, 637 nm, 640 nm and 642 nm respectively. The alkaline fading reaction in various solutions was followed at the respective maxima of the dye. SG, in aqueous media, obeys Beer's law upto 2.0×10^{-5} M ($E = 7.96 \times 10^4$). Therefore, the reaction was carried out at dye concentrations lower than this concentration. In order to avoid any complications due to the interference by backward reaction the hydroxyl ion concentration in the reaction system was taken in much excess to that of SG and the kinetic data were recorded in first few minutes of the reaction. The values of pseudo first

order rate constant under these conditions were reproducible within a range of $\pm 5\%$.

Effect of substrate concentration on rate

The effect of substrate concentration on the reaction rate was studied by keeping the parameters viz., temperature (25°C), hydroxyl ion concentration (0.02 M) and ionic strength (0.02) fixed and varying SG concentration (1.0×10^{-5} M to 1.8×10^{-5} M) in the reaction system. The results summarized in Table Ia show that under the condition of excess of alkali in the reaction system colour fading reaction of SG follows pseudo first order kinetics and thus rate constant is independent of substrate concentration.

Effect of reactant concentration on rate

The values of first order rate constant as a function of hydroxyl ion concentration (1.0×10^{-2} M to 5.0×10^{-2} M) which were obtained at fixed SG concentration at 25°C are summarized in Table Ib. Graphical analysis shows that the data conform to Eqn. (1) with the value of correlation factor, r , equal to 0.999:

$$k = k_1 + k_2 [\text{OH}^-] \quad \dots (1)$$

The values of k_1 and k_2 being 1.10 and $3.40 \text{ l.mol}^{-1}\text{min}^{-1}$ respectively.

Effect of ionic strength in water and in organic solvent-water mixtures

The influence of ionic strength on the reaction rate was studied to determine the nature of reacting species and to evaluate the interionic parameters in water and in 30% (v/v) and 40% (v/v) acetone-water mixtures. The studies were done at 25°C at fixed concentrations of hydroxyl ion (2.0×10^{-2} M) and SG (1.6×10^{-5} M). Ionic strength was varied by adding necessary amount of KNO_3 when the reaction was carried out in water ($\mu = 2 \times 10^{-2}$ to 1.42) and in acetone-water mixtures ($\mu = 2 \times 10^{-2}$ to 0.66). The rate constant was found to decrease with increasing ionic strength (Fig. 1). The data were subjected to analysis¹⁷ according to Bronsted Eqn. (2) which gave in-conclusive results;

$$\log k' = \log k'_0 + 1.02 Z_A Z_B \quad \dots \quad (2)$$

where k' is second order rate constant, k'_0 is rate constant at zero ionic strength and $Z_A Z_B$ is the product of charges carried by reacting species. It was observed that in the plot of $\log k'$ vs μ the points corresponding to higher values of μ do not lie on the straight line (Fig. 1) suggesting the nonapplicability of Eqn. (2). However, the straight lines drawn upto lower values of μ gave the values of $Z_A Z_B$ equal to -0.50, -0.77 and -0.60 in water, 30% (v/v) acetone-water and 40% (v/v) acetone-water mixtures. It may be inferred from these values of $Z_A Z_B$ that oppositely charged species are involved but the magnitude of charges on the reacting species could not be predicted.

The application of Debye-Hückel¹⁷ Eqn. (3)

$$\log k' = \log k'_o + \frac{1.02 Z_A Z_B / \mu}{1 + \sqrt{\mu}} \quad \dots (3)$$

linear plots over a wide range of μ (Fig. 1). The values of $Z_A Z_B$ obtained from the slope are listed in Table 2. Since these values still deviate from unity the data were analyzed according to Bronsted-Christiansen¹⁷ Eqn. (4)

$$\log k' - \log k'_o + \frac{2 A Z_A Z_B / \mu}{1 + \beta a_i / \mu} \quad \dots (4)$$

where β and A are Debye-Hückel constants and a_i is an interionic parameter.

The value of a_i was computed by successive trial method⁵ by putting different values of a_i in Eqn. (4) and observing its effect on the plot of $\log k'_o$ vs $\sqrt{\mu}$. According to Eqn. (4) the plot which is linear and parallel to $\sqrt{\mu}$ axis gives the correct value of a_i (Fig. 2). Taking these values of a_i , $\log k'$ was plotted against $2 A \sqrt{\mu} / (1 + \beta a_i / \mu)$. This was found to give plots (Fig. 3) with the values of slope equal to $Z_A Z_B$ which were found to be nearly unity (Table 2). These results suggest that the alkaline fading reaction of SG involves reactants which carry unit charges of opposite sign. It may be pointed out here that the physical meaning of interionic parameter a_i is not well defined except one may only suggest from the results that the dye ion is more or less solvated in solvent-water mixture than

in water. The lower value of a_i in solvent-water mixtures than in water is in agreement with the earlier findings of Sinha and Katiyar.⁵

Effect of dielectric constant on rate

The applicability of Bronsted-Christiansen-Satchard¹⁷ Eqn. (5) was tested for this reaction:

$$\ln k'_o = \ln k_o - \frac{Ne^2 Z_A Z_B}{DRT \cdot r} \quad \dots (5)$$

$D = \infty$

where D is permittivity of the medium; All other terms have their usual meaning.¹⁵

The values of first order rate constant were determined in acetone-water, dioxane-water and ethylene-glycol-water ($D < 50$) isocomposition mixtures at fixed concentrations of hydroxyl ion¹⁷ (0.01 M) and SG ($1.6 \times 10^{-5} \text{ M}$). The plots of rate constant $\text{vs } \frac{1}{D}$ in various solvent-water mixtures are not straight line (Fig. 4) suggesting the nonapplicability of Eqn. (5). In case of acetone-water and dioxane-water mixtures the rate constant initially shows a decreasing trend and after passing through a minimum it starts increasing with increasing solvent percentage in the reaction system. In case of ethylene-glycol-water mixture the plot of rate constant $\text{vs } \frac{1}{D}$ initially rises steeply but afterwards gradually with increasing solvent concentration. These results suggest that at lower percentage of solvents specific effects are important whereas at higher solvent concentration effects due to decrease in

dielectric constant of the media override the specific solvent effects.¹⁸

Effect of temperature on rate

The effect of temperature on the reaction rate was studied to (i) evaluate the values of thermodynamic activation parameters of the reaction, (ii) to find out the influence of dielectric constant on the values of activation parameters and (iii) to investigate the dependence of the quantities of activation on ionic strength. Consequently, the values of rate constant in the temperature range of 293°K to 318°K were recorded in water, in 5%, 10%, 15%, 30% and 40% (v/v) acetone-water mixtures and in 5%, 10% and 16% (v/v) dioxane-water mixtures. Studies were done at two ionic strengths viz., 0.01 and 0.4 in water and in 30% (v/v) and 40% (v/v) acetone-water mixtures. The concentrations of the reactant (0.01 M) and substrate (1.6×10^{-5} M) in all the studies were kept constant. The values of rate constant so obtained in various media were plotted against $1/T$ to obtain the values of ΔE^\neq . Illustrative plots in 30% (v/v) acetone-water mixtures at two ionic strengths are shown in Fig. 5. Other parameters were obtained utilizing following Equations:⁵

$$\Delta F^\neq = 2.303 RT (\log \frac{RT}{Nh} - \log k') \quad \dots (6)$$

$$\Delta S^\neq = 2.303 R (\log Z - \log e \cdot \frac{RT}{Nh}) \quad \dots (7)$$

$$\Delta H^\neq = F^\neq + T\Delta S^\neq \quad \dots (8)$$

$$\text{and } \log Z = \log k' + \frac{\Delta E^\neq}{2.303 RT} \quad \dots (9)$$

The values of the thermodynamic activation parameters in various media are summarized in Table 5. Certain characteristic features of these parameters in various media obtained from the data (Table 5) are described below:

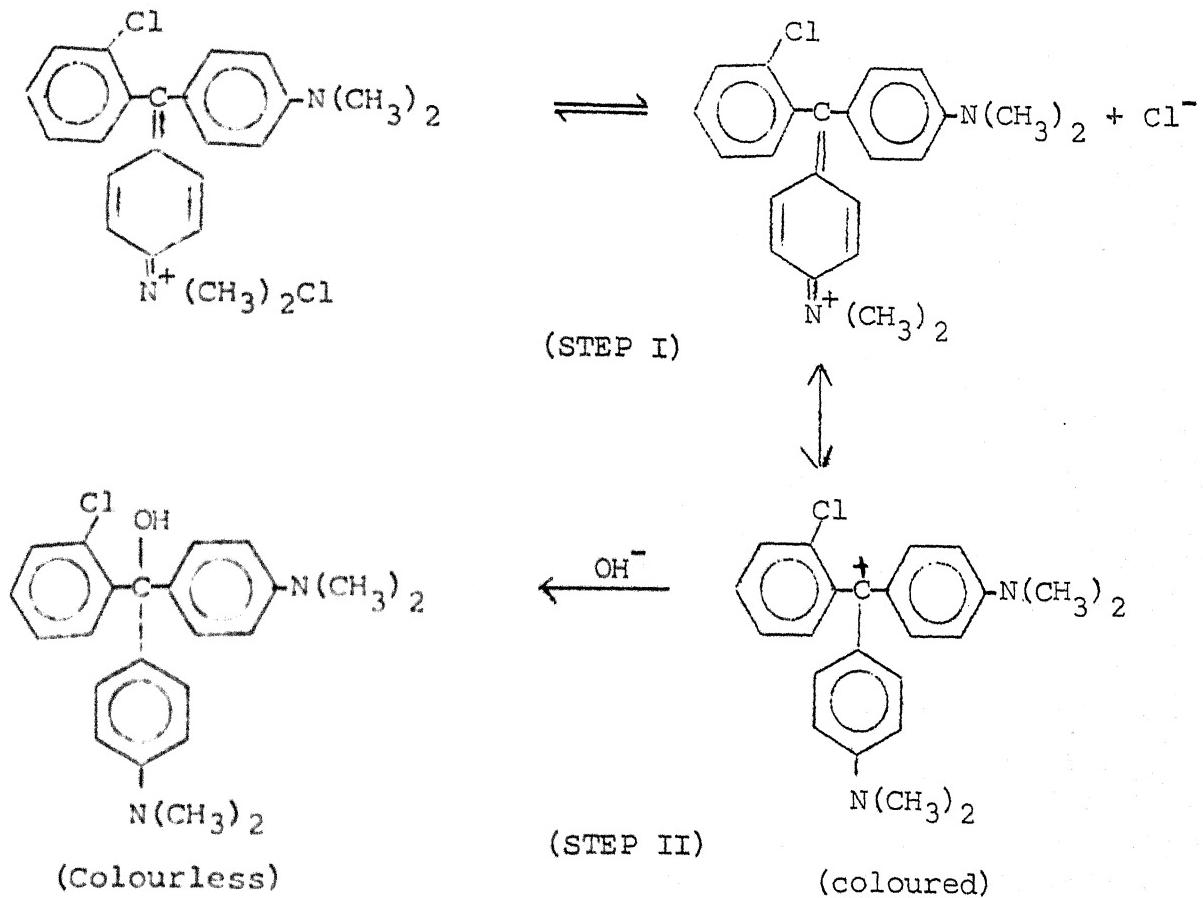
(i) The value of entropy of activation, ΔS^\neq is negative in water as well as in organic solvent mixtures. (ii) The value of energy of activation, ΔE^\neq , decreases with increasing ionic strength in the reaction system in water and also in acetone-water mixtures. (iii) The value of energy of activation, ΔE^\neq , increases with increasing solvent percentage at a given ionic strength. (iv) The value of frequency factor Z at a given ionic strength increases with increasing solvent percentage. (v) The values of enthalpy of activation ΔH^\neq and also that of entropy of activation first decreases (at $\mu = 0.01$) and then starts increasing with increasing solvent percentage in the reaction system and (vi) the difference between the values of entropy of activation, ΔS^\neq , at higher ionic strength and at lower ionic strength is negative in water and also in acetone-water mixtures.

These results, on the basis of analysis proposed by LaMer,¹ establishes beyond doubt that the alkaline fading reaction of setoglaucine involves oppositely charged species. This is confirmed by the effect of ionic strength on the reaction rate. The observations that Z factor as well as ΔE^\neq increases with

increasing solvent percentage is in agreement with the observation of specific solvents effects. As the percentage of solvent in the reaction system increases, this results in the decrease of dielectric constant of the medium making the probability of collisions of the reactants higher which is observed in the form of increased value of Z. However, specific effects i.e., selective¹⁸ solvation by solvent molecules may block the reaction site which results in an increase in the activation energy of the reaction. Thus, these two competing phenomena are presumably involved in determining the overall effect of a given solvent. This agrees with the effect of organic solvents observed in this reaction.

The comparison of thermodynamic parameters of the reaction in presence of acetone-water and dioxane-water mixture under the condition of same dielectric constant shows (Table 5) that the value of ΔE^\neq , and Z in acetone water-mixture is higher than the value in dioxane-water mixture. The value of ΔE^\neq in two media at same D and μ suggest that SG ion is more solvated by acetone than by dioxane molecules. The trend in the value of Z factor in two media may also have contribution from the effect of viscosity.¹⁷ The results are further confirmed by the fact that the value ΔS^\neq in dioxane-water mixture is more negative compared to the value in acetone-water mixture under similar conditions of D and μ . The higher negative value in presence of dioxane-water mixtures compared to that in acetone-water mixtures suggests that the charge of SG ion is more exposed for interaction with hydroxyl ion in the former media.

On the basis of these studies following mechanism may be proposed for the alkaline fading reaction of setoglaucine;



Step I involves fast ionization of the dye to give carbonium ion which reacts with hydroxyl ion at slow measurable rate in step II.

Table 1. Variation of pseudo first order rate constant, k_ψ , as a function of the concentrations of: 1a, substrate, SG and 1b, reactant, OH^- for the alkaline fading reaction of setoglaucine at 25°C

1a		1b	
$[\text{OH}^-] = 2.0 \times 10^{-2} \text{ M}$	$[\text{SG}] \times 10^5$	$[\text{OH}^-] \times 10^2$	$k_\psi \times 10^2 \text{ min}^{-1}$
1.0	7.83	1.0	4.48
1.2	7.91	2.0	7.84
1.4	7.97	3.0	11.08
1.6	7.87	4.0	14.73
1.8	7.92	5.0	18.09

Table 2. The values of $Z_A Z_B$ and a_i for the alkaline fading reaction of SG in water and in acetone-water mixtures at 25°C

Medium	Values of $Z_A Z_B$ by different plots ($\log k'$ vs)			Interionic parameter, $a_i, \text{Å}$
	$\sqrt{\mu}$	$\sqrt{\mu}/(1+\sqrt{\mu})$	$2 A \sqrt{\mu}/(1+\beta a_i \sqrt{\mu})$	
Water	-0.50	-0.99	-1.00	2.6
30% (v/v)				
Acetone-Water Mixture	-0.77	-0.79	-0.89	1.6
40% (v/v)				
Acetone-Water Mixture	-0.60	-0.71	-0.88	1.6

Table 3. Thermodynamic quantities of activation at 25°C for alkaline fading reaction of setoglaucine in various media.

Medium	D	ΔE^\neq	Z	ΔF^\neq	$-\Delta S^\neq$	ΔH^\neq
<u>Water</u>	0.01	13.47	1.67×10^{11}	21.32	16.63	16.35
	0.40	12.52	3.65×10^7	21.91	33.49	11.93
<u>Acetone + Water</u>						
5% (v/v)	0.01	76.00	14.82	3.73×10^9	21.45	28.85
10% (v/v)	0.01	74.00	15.10	4.89×10^9	21.57	23.68
15% (v/v)	0.01	71.60	15.35	9.15×10^9	21.45	22.45
30% (v/v)	0.01	64.25	16.58	2.26×10^{11}	21.14	16.03
30% (v/v)	0.40	64.25	14.97	2.90×10^9	21.77	24.75
40% (v/v)	0.01		17.90	1.46×10^{12}	20.96	12.29
40% (v/v)	0.40		15.66	1.27×10^{11}	16.03	17.18
<u>ioxane + Water</u>						
5% (v/v)	0.01	74.00	14.73	1.12×10^9	16.99	26.65
10% (v/v)	0.01	69.30	14.97	4.81×10^9	18.70	23.73
16% (v/v)	0.01	64.25	15.20	8.79×10^9	21.31	22.57

Units: ΔE^\neq : kcal mol⁻¹; Z : l.mol⁻¹s⁻¹; ΔF^\neq = kcal K⁻¹mol⁻¹;

ΔS^\neq : cal K⁻¹ mol⁻¹; ΔH^\neq : kcal mol⁻¹.

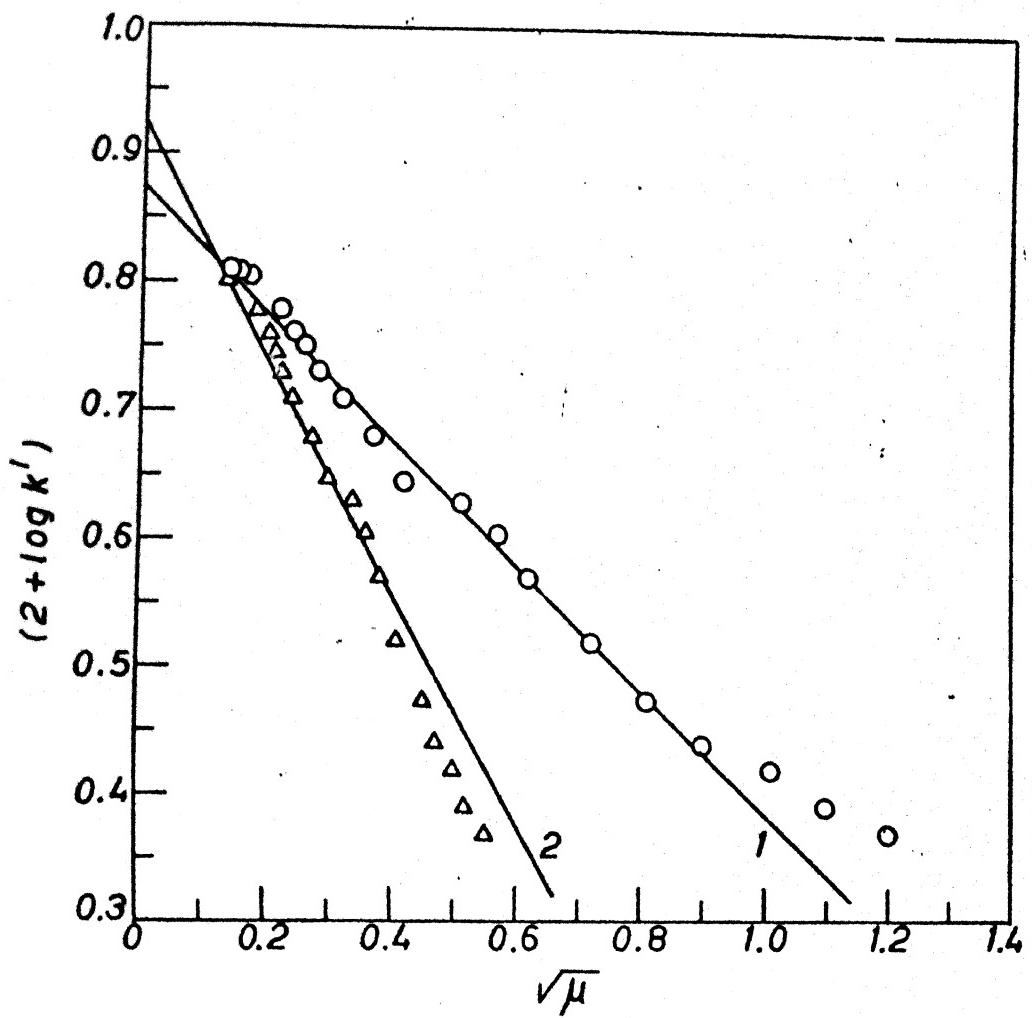


Fig. 1. Variation of plot (1); $\log k'$ vs $1/\sqrt{\mu}$ plot (2);
 $\log k'$ vs $1/\sqrt{\mu}/(1 + 1/\sqrt{\mu})$ for the alkaline fading
reaction of SG.

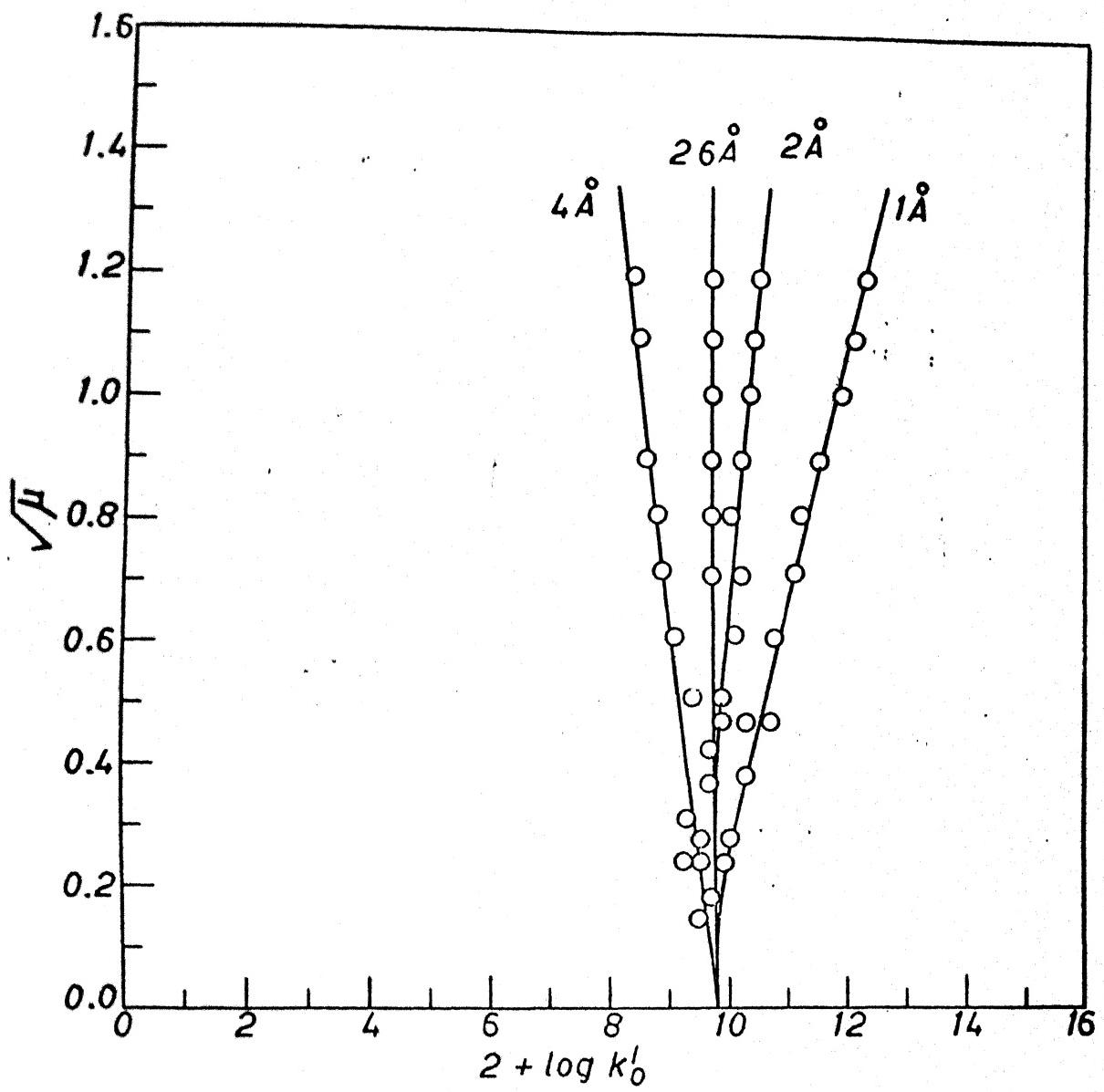


Fig. 2. The effect of a_1 upon the plot of $\sqrt{\mu}$ vs $\log k'$ for the reaction of setoglaucline with hydroxyl ion.

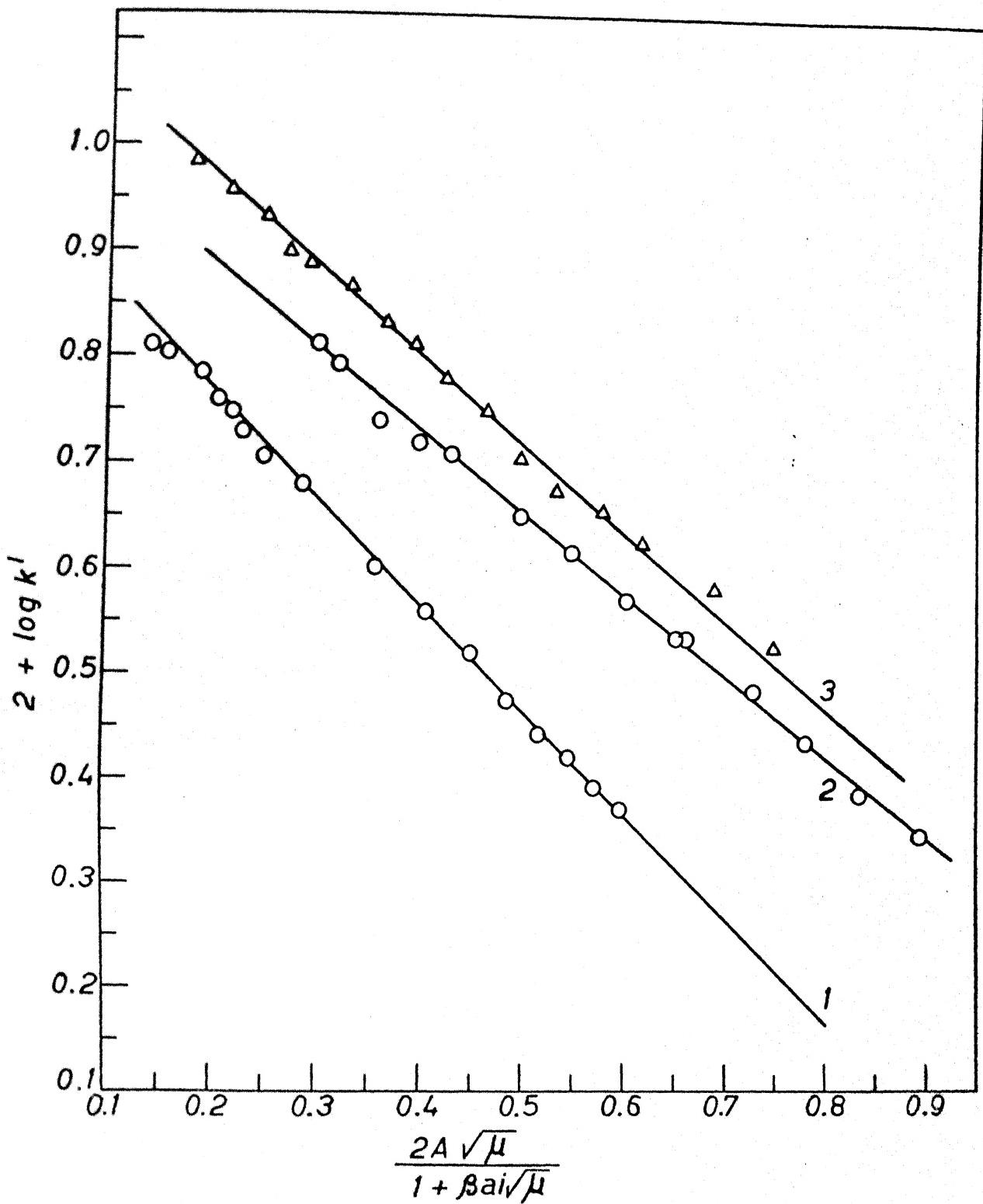


Fig. 3. Determination of the value $Z_A Z_B$ according to Equation (4) for the alkaline fading reaction of setoglaucine; plot (1): in water; plot (2): in 30% (v/v) acetone-water mixture and plot (3): in 40% (v/v) acetone-water mixture.

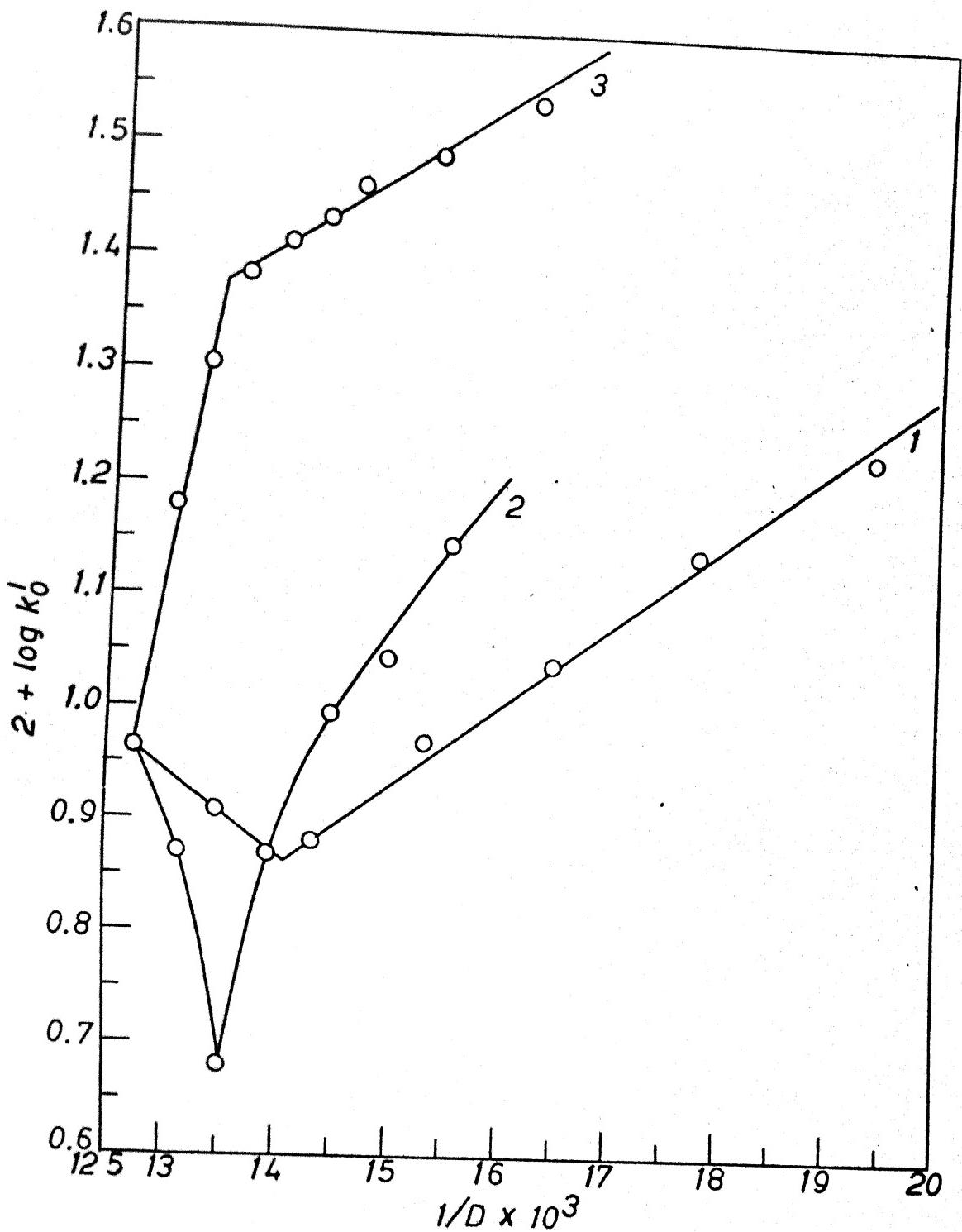


Fig. 4. The effect of dielectric constant on the reaction rate for alkaline fading reaction of setoglaucine; plot (1): dioxane-water; plot (2): acetone-water; and plot (3): ethylene glycol-water mixtures.

$\log k'$

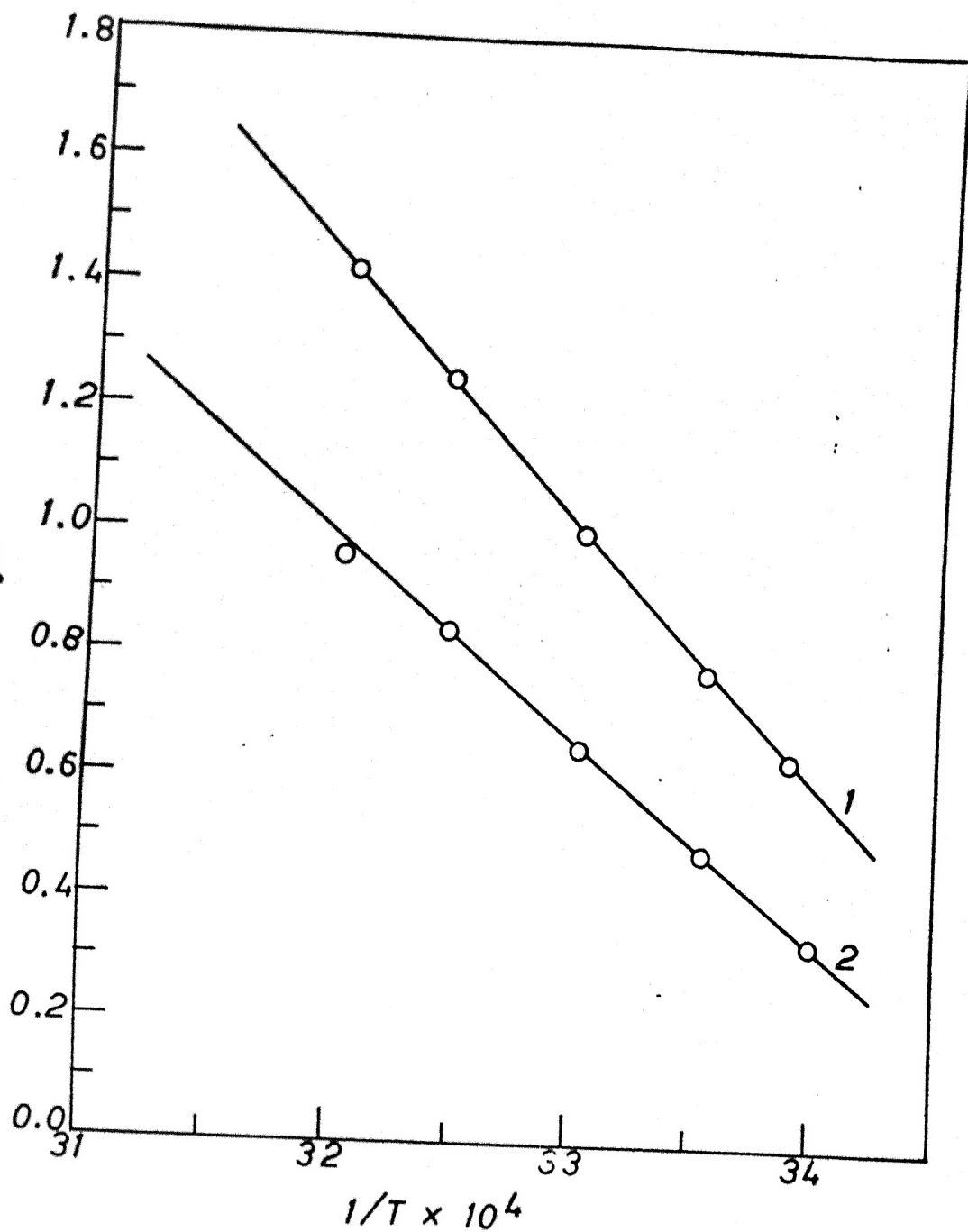


Fig. 5. Arrhenius plots for the reaction of SG⁺ carbonium ion with hydroxyl ion in 30% (v/v) acetone-water mixture; plot (1) and plot (2) correspond to $\mu = 0.01$ and 0.4 respectively.

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LIST OF PUBLICATIONS

1. Micellar Effects on the Reaction of Carbonium Ions with Nucleophiles: Alkaline Fading of Brilliang Green,
K.L. Patel and Sarvagya S. Katiyar,
Nat. Acad. Sci. Lett., 1, 143 (1978).
2. Catalytic Effects on the Reaction of Carbonium Ions with Nucleophiles: Alkaline Fading of Setoglaucine
K.L. Patel and Sarvagya S. Katiyar,
Fundamental Research in Homogeneous, Vol. 3,
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3. Kinetic Studies on the Reaction of Carbonium Ions with Nucleophiles: Alkaline Fading of Setoglaucine,
K.L. Patel, S.K. Srivastava and Sarvagya S. Katiyar
J. Ind. Chem. Soc. (submitted).
4. A Formulation of Reaction Kinetics in Presence of Micelle-forming Surfactants,
K.L. Patel and Sarvagya S. Katiyar,
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5. Micellar Catalysis,
K.L. Patel and Sarvagya S. Katiyar,
Ind. J. Chem. (submitted).
6. Micellar Effects on the Reaction of Carbonium Ion with Nucleophiles: Influence of Solvents,
K.L. Patel and Sarvagya S. Katiyar,
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7. Analysis of Counter Ion Effects on the Reaction of Carbonium Ions with Nucleophiles,
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J. Phys. Chem. (submitted).

Presentations

1. "Micellar Effects on the Reaction of Carbonium Ions with Nucleophiles: Alkaline Fading of Malachite Green," Annual Meeting, Nat. Sci. Acad. (India), Shilong, 1978.
2. "Catalytic Effects of Micelles," 1st International Conference on Homogeneous Catalysis," Corpus Christie, Texas, U.S.A., 1978.
3. "A Treatment for the Analysis of the Effect of added Counter Ions on the Micelle-Catalysed and Inhibited Reactions," 3rd International Conference on Surface and Colloid. Sci., Stockholm, Sweden, 1979.
4. "Effect of Organic Solvents on the Micelle-Catalysed and Micelle-Inhibited Reactions, 27th I.U.P.A.C. Conference, Finland, 1979.

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VITAE

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